MODERN ELECTRO-PLATING

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MODERN ELECTRO-PLATING

A GUIDE-BOOK FOR PLATERS WORKS CHEMISTS, & ENGINEERS

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FOREWORD

THIS little book is not a *text-book*: it is not intended to be. It consists, essentially, of a number of articles on the Electro-deposition of Metals that have appeared from time to time in *Beama*, and to the editor of this journal the author is much indebted for permission to reproduce the articles in book form.

The author's object in seeking republication is to help still further those who may feel need of assistance in their work connected with the deposition of metals. It is desired to assist foremen platers, works chemists, and engineers, especially. In order to do so as far as possible the author has *omitted* much. The subject-matter has been carefully chosen, and those metals only have been considered which are of most general interest. Silver might, perhaps, have been included, but economy of space did not permit of this.

The author has stepped out of the rut that text-books on Electroplating follow, and he has endeavoured to treat his subjects from a fresh point of view. He has not hesitated to insert his own practical experience. A familiar and conversational style of expression has been deliberately adopted. The author has wished to "talk" to the reader: but if he has not, even so, made plain that which he intends to convey, there still remains a partial remedy. If any one does not understand this or that in the book, *and he seriously wishes to do so*, let him communicate his trouble to the author. His letter will be received with pleasure. The author will be only too glad to resolve doubts: he considers it a moral obligation to do so. It is an author's duty to make clear his meaning—not to puzzle his reader with linguistic conundrums.

CONTENTS

PAGE

I. A GENERAL REVIEW . 1

II. THEORY . . . 10

III. PRACTICE: THE PREPARATION OF THE WORK . 21

IV. PRACTICE: THE DEPOSITION PROCESS AND THE FINISHING PROCESS . 31

V. IRON 45

VI. NICKEL 57

VII. ZINC 69

VIII. LEAD 85

IX. TIN AND CHROMIUM 97

X. COPPER 111

XI. THE STRUCTURE OF ELECTRO-DEPOSITED METAL . . . 128

XII. ON READING 144

TABLES 147

INDEX 157

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CHAPTER I

A GENERAL REVIEW

THE applied science of electro-metallurgy may be conveniently divided into (1) Electric furnace work, and (2) Electro-deposition; and the latter is broadly divisible into (i) Electro-refining, and (ii) Electro-plating. This book deals almost entirely with electro-plating, which has secured a firm footing in the industry of the country.

(i) ELECTRO-REFINING

While undoubtedly electro-plating is, in England, much more widely practised than any of the other divisions of electro-metallurgy, yet, just as certainly, considerable progress has of late years been made in electro-refining, not only elsewhere abroad, but also in the British Colonies. Crude copper and zinc are refined electrolytically in Australia and Tasmania; and it is interesting to note that, despite gloomy forebodings, zinc refining is now a commercial proposition. There is no doubt that the great obstacle to the development of an electro-refining industry in this country is the cost of power. Copper is the only metal that has been seriously considered at all in this country; and with one or two notable exceptions, as, for example, the pioneer work of the Elliott Metal Co., even the electro-refining of copper has been left alone. The market prices (in London) of ordinary "Standard," and of electrolytic copper, respectively, show that the margin is not sufficiently great to induce English capitalists to sink the capital outlay necessary—at any rate for small-scale operations.

Some remarks recently made by Mr. S. Field, whose work on the electrolytic extraction of zinc is well known, are instructive. He says:[1] ". . . it should be remembered that no large scale or commercial plant has yet been put down in this country. Certain experiments carried out in South Wales by one of the zinc firms produced between 100 and 200 tons of the pure metal. Then the experiments closed down with a view to building upon a more convenient site and on a very much larger scale.

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[1] "Electro-deposition and Electro-plating," reprinted from the *Trans. Far. Soc.*, 1921, vol. xvi. p. 492. See p. 31 of the reprint.

You could not produce electrolytic zinc commercially in this country with a plant of 1½ tons a day capacity; the nearer it gets to 20 or even 100 tons a day the better the prospect will be."

But there is hope. It seems that German movements in Devonshire before the war have led to the consideration by a syndicate of the proposition of copper-refining by electrolysis in that county. It is proposed to lay out a large sum (some millions) in electrical plant, which will be used, in considerable part, to supply energy for refining purposes. Water-power not being available, the lignite beds existing in the country will be made the source of cheap power. The chairman of the syndicate is a well-known Midland manufacturer. Commenting briefly on the scheme, Professor H. C. H. Carpenter, F.R.S., says:[1] "In the years immediately preceding the war, the United States of America refined electrolytically more than 90 per cent. of the world's output of pure copper. Most of this production was absorbed by the electrical industry. Great Britain, accordingly, was obliged to obtain the bulk of this type of copper from America, and in 1913 imported about 100,000 tons." It is to be hoped that this project will succeed.

Things are different abroad, including the British Dominions, at places where water-power is available. The electro-refining of zinc has become, of recent years, an established industry in Australia and Tasmania—to mention only British Possessions. And the introduction of the process into Burmah has, the writer understands, already been made. That it will ever be commercially possible to adopt electrolytic methods in this country (in the case of zinc) is, at present, questionable. As Mr. Field points out, it certainly could not be done with a small plant. But if the scheme for copper-refining above mentioned were to succeed, then it might become quite possible to treat zinc as well.

Theoretically, the process of electrolytic refining is simple enough, though in practice things are not so simple. It consists of the transfer of the metal (copper, zinc, or other), by electrolytic means, from a sheet of impure to a sheet of pure metal. The two sheets of metal are suspended in an aqueous solution of some salt, usually the sulphate, of the metal to be refined; and the electric current is passed—from the source of current supply to the impure sheet (called "the anode"), on from the anode, through the solution, to the pure sheet (called "the cathode"),[2] and then on from the cathode to the source of current. Most of the impurities in the anode (the soluble sheet) either fall to the bottom of the vat that contains the solution, or are held in solution, if they are soluble, and prevented, by taking proper precautions, from being deposited with the copper or zinc (or other metal) upon the cathode sheets. The purity of the refined metal is frequently as high as 99·98 per cent. and 99·99 per cent.

Lead and iron are two other metals that are refined electrolytically, on a considerable scale, in the United States of America. But nothing has been attempted in this country.

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[1] *Nature*, Feb. 19, 1920.

[2] In zinc-refining and zinc-extraction it is not unusual to use sheets of aluminium as cathodes.

(ii) ELECTRO-PLATING

Electro-plating is the branch of electro-metallurgy that has been most extensively developed in this country. The silver-plating trade of Sheffield and Birmingham and the nickel-plating industry of the Midlands are world-famous. Nevertheless, the present stage of development, whether in regard to silver, nickel, or other metal, so far as "process" is concerned, is twofold: While (1) the process or processes employed are, in general, at least the equal of those employed elsewhere, yet (2) they are not, by much, what they ought to be.

It may be conveniently stated in this place that the general procedure in electro-plating is similar to that in electro-refining, namely, transfer of metal from anode to cathode by the agency of the electric current. In the case of electro-plating, however, the cathode (the article deposited upon) is some object—a spoon, fork, or the like, some cycle or motor fitting, and so on—which may or may not be of the same kind of metal as the deposit. Furthermore, the object of electro-plating is different. It may be decorative—to make an "ugly" metal look pleasing; or it may be protective, as in electro-galvanizing; or, again, it may be both decorative and protective, as in the case of much nickel-plating.

In this chapter, silver, nickel (and cobalt), zinc, copper, and iron are considered individually, as being the most important; only a few words are given to the remainder.

(a) *Silver*[1]

The "process" of silver-plating is to-day essentially the same as it was sixty years ago. The same highly-poisonous solution of the double cyanide of silver and potassium is used; the same slow rate of deposition obtains; and the same old-fashioned methods of working are employed. With the exception of a few mechanical devices for keeping in motion the articles that are being plated, no innovations or important improvements have been made.

(b) *Nickel and Cobalt*

1. *Nickel.* The position is somewhat better in regard to nickel. Up to the year 1908 the solution used for nickel-plating consisted of the double sulphate of nickel and ammonium dissolved in water. This was the solution patented in this country by Dr. Isaac Adams in 1869 and 1870, and which was really a modification of Böttger's solution. It contained but little nickel (metal); and, in the case of "still" vat work (that is, where neither the solution nor the articles being plated are mechanically moved), the current density employed was small—not more than 3 ampères per square foot of surface. Hence, for nearly forty years no progress of any account had been made. In 1908 a development

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[1] Only a passing reference to silver is made. This metal will not be considered separately and individually in this book, since it is not one of prime importance in engineering.

occurred, which was occasioned by the threat of foreign competition. A solution of a wholly different type from the "double salts" (nickel ammonium sulphate) bath was introduced from abroad in or about the year 1908. This solution consisted primarily and mostly of the "single salt" of nickel (nickel sulphate). The result was that since the "single" salt is very much more soluble than the "double," and contains a much greater percentage of nickel, the solution could be made much more concentrated in metal, and, as a consequence, the rate of deposition could be greatly increased—for "still" vat work it was more than doubled. Such a bath, giving as it did, equally as good and in some respects better deposits of nickel, affected output as regards both quality and quantity. The spur thus applied by foreign competition (supported, as it was, by both money and scientific procedure) had a beneficial effect upon the whole of the nickel-plating industry of the country. Baths of similar type to the foreign product were, as a result of research work, placed on the market by British manufacturers, and soon succeeded in checking the foreigner's career. The advance from the scientific point of view was, that nickel-plating began to be looked upon as a matter deserving of scientific research. As regards the solutions used, however, practically no further development has occurred. In a recently published work,[1] edited by Dr. J. N. Friend, two recipes for nickel-plating solutions are given, which represent, presumably, what the author imagines to be the latest word on such solutions. Both contain the old-fashioned "double salt"; one is said to work at 5 amp./ft.^{2} and the other at 10 amp./ft.^{2} The writer has reasons for believing that neither of these solutions is known to any extent outside the laboratory. Nor is either of them likely to be so. It is a scientific impossibility for any bath containing nickel "double salts" to compete with the "single salts" solutions. The advances which remain to be made (and they are many) will be in the direction of the development of "single salts" solutions. Indeed, research is now being conducted along the lines indicated, with the result that several baths have been composed that can be worked at more than twice the rate possible with any solution now on the market. Moreover, the deposition can continue *uninterruptedly* for a week or more and deposits obtained that measure over one-fifth of an inch in thickness.

Nickel-plating is applied to a very large number of articles, among the chief of which may be enumerated those belonging to the following: Cycle and motor parts, sanitary fittings, gramophone parts, toys, electrical fittings, and saddlery and harness furnishings. This variety of appliance shows the importance of the industry; and this is emphasized by the fact that, although the average thickness of the deposit (even on the best plated cycle or motor part) does not much exceed $2\frac{1}{2}/1000''$ (it is often much less), yet some 500 tons of metallic nickel are consumed annually in England for nickel-plating purposes.

2. *Cobalt.* This is a much-neglected metal. The neglect may be due in part to the comparatively high cost of the metal in pre-war days; but it is undoubtedly partly due to (i) lack of initiative and enterprise, and (ii) unfamiliarity with the properties of the metal and the possibilities

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[1] *Text-book of Inorganic Chemistry,* 1920, vol. ix. part 1.

of its use. At the present time there is no excuse for the latter. The production, physical and chemical properties, and possible applications of cobalt, have been studied recently by the metallurgists of the Canadian Government, and the results of their researches are embodied in a series of publications issued by the Mines Branch of the Department of Mines, Ottawa, Canada.[1] The conclusions of Dr. H. T. Kalmus and his collaborators on the subject of the comparative merits of nickel and cobalt for plating purposes are to the effect that, on account of its greater hardness and its advantages in regard to some other physical properties, deposited cobalt is preferable to deposited nickel. Moreover, the rate of deposition of cobalt from its solutions can be much greater than that of nickel from baths of analogous composition. It may be mentioned, in relation to what has been said above about "single" and "double" nickel salts, that Dr. Kalmus indicates that solutions made up of "single" cobalt salts (that is, for instance, cobalt sulphate) are many times faster in working than those based upon the "double" salts of cobalt (that is, those containing ammonia). An interesting and important fact is, that the results of the researches made and the conclusions reached, as embodied in the reports referred to, have been applied and confirmed, respectively, in actual works practice and on a considerable scale.

(c) *Zinc*

Electro-plating with zinc is used only for protective purposes. It is employed to coat iron articles, and so protect them from the natural agencies of corrosion—atmosphere, sea-water, and others. The process is termed *electro-galvanizing*, in contra-distinction to the hot or pot-galvanizing method of protecting iron.

Electro-galvanizing is gradually becoming more and more adopted as its merits become better known. The process has had to fight prejudice and inertia, as well as to justify its existence in the matter of cost. A hopeful feature is that, during the few years preceding the war, electro-galvanizing was gaining ground in the Glasgow and Falkirk districts in Scotland. Outplaters in these districts (by "outplaters" is meant those who do not themselves manufacture the goods, but receive them from others to plate—their business is electro-plating simply) found themselves able to make satisfactory profits on the electro-galvanizing of such cheap and crude articles as hot-water boshes, air-bricks, conduit pipes, and large bolts and nuts. During the war much use was made of electro-galvanizing for protecting sea-planes and mines from the corrosive action of sea-water. In general, it may be said that, while its employment in this country is very limited as compared with its use in America and on the Continent, electro-galvanizing is steadily gaining ground here. It is somewhat regrettable that its advocates should allow their enthusiasm to outrun their discretion. The use of electro-galvanizing as a means of protection has its limits; its range of application is also limited. For instance, steel springs, cycle spokes, and, in general, articles subject to tension, are likely to be harmed by the operations of electro-galvanizing. And further, this method is not likely to compete successfully, in the matter of cost, with the hot process in the case of metal sheet. The justifiable applications of electro-galvanizing are sufficiently numerous. To the articles mentioned above there may be added: The inside of steel tubes in order to facilitate the detection of flaws; wire strip for flexible tubing, corset fittings, nuts, bolts, and washers of all sorts and sizes, sad-irons and hardware of similar description; and many more.

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[1] *Reports*, Nos. 259, 309, and 334.

In its scientific aspect, zinc-plating has had much attention paid to it—*outside* this country. The researches of Heyn and Bauer in Germany, and of Cushman, Burgess, Sang, and others in America are well-nigh classical. But research on the subject is urgently needed, here and elsewhere, for the matter is bound up with the great question of the corrosion of iron and steel and its prevention. It is, however, safe to say that without scientific research and control (at present conspicuous by its absence), electro-galvanizing will be long before it comes into its own.

(*d*) *Copper*

From both the electro-chemical and electro-metallurgical points of view, copper has had more attention devoted to it than has any other metal, and the same remark holds good as regards both pure and applied research and commercial application. F. Förster and his pupils led the van of pure research, and G. Gore, Elmore, A. Watt, and others, in this country, and Roseleur in France, are entitled to claim front rank as regards commercial application.

The developments made during the last thirty and more years in copper-plating have reference rather to its application than to its means of accomplishment. With the possible exception of the copper sulphate and perchloric acid solution of F. C. Mathers, the ordinary copper sulphate and sulphuric acid bath is still without a rival; and it is not easy to see in what respects its perchloric acid rival is superior. The ordinary "acid copper bath," made up of sulphuric acid and copper sulphate in proportions suitable for the particular work it has to do in each case, will be very hard to oust from its position of supremacy. Nor is there any reason why it should be. Its adaptability, simplicity, and cleanliness make it economical to work and certain in its results. Research into copper deposition should be directed to the substitution of some other solution for the noxious and difficult-to-work cyanide of copper solution that is, at present, indispensable for certain purposes. So far as the writer is aware, nothing serious has been attempted—much less done—to that end. The cyanide of copper bath must be used where iron (and some other metals) have to be copper-plated, since, if such goods were suspended in the acid copper bath, without having a coating of copper already upon them, the acid would attack the surface of the metal, and the deposit would not adhere. The cyanide bath is also largely used for depositing a very thin layer of copper on various classes of goods that, for purposes of decoration, have to be "oxidized," as it is termed. Such articles are: Chandelier and lamp fittings, fenders, and fender ornaments, telephone and other electrical appliances, buckles and fancy goods, and innumerable other things. These (which may consist of iron, brass, or other metal) are given a deposit of copper of some fifteen to thirty minutes' duration in the cyanide bath, then dipped in sulphide of potash (or ammonia) solution in order to turn them blue or black, and then "relieved,"—that is, the sulphide coating on the copper is removed in places, usually by mechanical means. The result is called "oxidized copper"; it is really "*sulphurized*" copper. Since the cyanide solution is nearly always used hot—about 120° Fahr.—the fumes that are evolved cannot but be injurious to the health of the workers. And further, the bath is very wasteful, and it cannot with any ease or certainty be kept under control. Here is room for much research.

To direct attention to the extension of application of the acid copper bath, one has only to mention the following instances: Deposition of water-jackets for aeroplane cylinders, of seatings for the liners of engine cylinders, of the internal and external coatings of wireless condenser tubes and of radiator tubes (recently made successfully by deposition). The foregoing are more recent applications; those already in operation are too numerous to mention. In every case some variation of a standard bath of the following composition can be employed. The variation to be made is empirical and depends on the particular case; but as a standard bath, useful, without variation, for many purposes, the following is very serviceable:

2 lb. copper sulphate (commercially pure and arsenic free),
6 oz. (fl.) sulphuric acid, pure (spec. grav. = 1820),
1 gal. water.

(*c*) *Iron*

The present position of iron-plating is favourable, but the utility of the process is, so to say, on trial. The war has given it an impetus and, moreover, has disclosed the neglect of it in this country. Its war development is due to its employment in "building up" worn parts of aeroplanes and, to some extent, of armament. It was quicker and cheaper to "build up" such worn and, consequently, undergauge parts than to supply new ones. By this means a worn crank-shaft, say, that cost anything from £60 upwards, could be made usable for a very few pounds. Unpreparedness, due to lack of encouragement of research, was, however, early apparent. Those engaged, including those in charge, had little or no idea as to how to proceed to obtain thick deposits of iron by continuous deposition, and as little was known about the scientific control of the processes employed. Indeed, it may safely be said that but little is known to-day, in this country at any rate, as to the actual physical nature of the deposits formed. But it must, in fairness, be stated that the Scientific and Industrial Research Committee of the Privy Council is encouraging a research into this last part of the subject. The laborious process employed in the Government workshops, both in France and England during the war, was to deposit 2 or 3 thousandths of an inch of iron, then a thin coat of copper, then another few thousandths of iron, and so on. It was only towards the end of the war that Lieut. Emtage, R.A.F., and others, showed the way to continuous deposition and the attainment of thick deposits in one operation. And this was so notwithstanding the fact that American scientific men had long ago shown how to obtain heavy deposits of iron, whether for refining or plating purposes.[1]

Though the difficulties of the deposition part of the process are now fairly well known, yet but little is known of the nature of the material produced—its structure, defects, and how far it can be case-hardened, heat-treated, and the like. One thing is certain, as the writer can prove positively by visual evidence, namely, that the article, when plated, cannot, or at any rate in most cases should not, be used unless and until it has received some kind of heat-treatment. But under scientific control, both of operation and examination of the product, and aided by heat-treatment, if and where necessary, iron-plating should have a great future before it, and find a large number of varied applications.

(f) *Tin, Lead, and Other Metals*

The metals considered in paragraphs (*a*) to (*e*) are the most important ones that are dealt with in the depositing shops of this country. The electro-deposition of tin, however, finds some application. Much of the so-called "silver-oxidized" work is really electro-tinned. Electro-deposited tin has also been used to renew the insides of biscuit boxes and culinary articles, and to "tin" meat skewers, hooks, and similar goods. But its application is not (comparatively) extensive. Lead and the remaining metals are even less used in the plating shop. One application of electro-deposited lead that might well be extended is the coating of battery nuts, bolts, and other metal parts by electrolysis. This would serve to protect such articles from the acid spray evolved when the cells are charging. Research on the application of all the metals comprised in this group has been almost neglected in this country since the days of Dr. Gore. The outstanding work (on the applied side), is that done by F. C. Mathers on lead and tin and by A. G. Betts on lead, in America. The work of each of these authors will be considered in the chapters on tin and lead, respectively.

CONCLUSION

It will be gathered from the foregoing that the general position, in this country, in the matter of that branch of applied electro-metallurgy that concerns the deposition of metals is, in the writer's opinion, by no means satisfactory. The reason for this is not far to seek. Apart from the question of power and cost, it can scarcely be denied that one cause of the unsatisfactory state of things is the lack of educational facilities. This will be evident, probably, from the statements that (1) there is only one University lecturer on electro-metallurgy in the country, namely, at Sheffield; and (2) there is only one technical school that concerns itself *at all seriously* with the subject, namely, that at Birmingham. Nowhere at all is such work done as has been carried out by Förster and his pupils. The consequence is that much of the work done in the shops is not under scientific control; methods and means are slow to advance; and new ideas often fall on barren soil. At the same time, experience and long use has taught our "practical" men to employ the present means at their disposal to such good effect that, as has been said already, the output of the Sheffield and Birmingham areas is world-famous, and this indicates clearly what might be done if scientific progress were encouraged and educational facilities were given.

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[1] For further general remarks, see "Electro-deposited Iron: Its Value for Engineering Purposes," *The Engineer*, Oct. 8, 1920; and "The Industrial Future of Electro-deposited Iron," *The Electrician* (Spec. Iron and Steel No.), Nov. 5, 1920.

Finally, it may be pointed out that the development of electro-metallurgy must lead to an extension of the application of engineering plant and machinery, both electrical and mechanical. The immediate source of power for electro-metallurgical operations is the dynamo, motor-generator, or the battery. Moreover, the skill of the mechanical engineer in the device of the means of carrying out this or that electro-metallurgical process is, not seldom, the factor upon which the success or failure of the process depends.

CHAPTER II.

THEORY

THE principal object of the present chapter is to assist engineers, especially, and others of equal standing who directly or indirectly may be in control of electro-deposition processes, whether refining or plating. The way in which it is proposed to do this is to set out, in general terms, just so much of the theory underlying such processes as enables one to supervise them with a scientific understanding, and thereby efficiently and economically, to control the operations of the workshop. Details will be avoided: the subject will be treated in a general way, so as to be applicable, not to this or that particular one, but to all metals.

THE LAWS OF ELECTROLYSIS

The two most important natural laws with which the electro-metallurgist must be familiar are: OHM'S LAW and FARADAY'S LAWS. Together with these he must be acquainted to some extent with what is termed THE IONIC THEORY.

A knowledge, even partial, of this theory, enables one to form a mental picture of the mechanism of the electro-deposition process, and to account for the phenomena connected with it. The theory may or may not be wholly accordant with all the facts: at the very least it is a useful tool. It answers much the same purpose to the electro-metallurgist as the conception of the ether and, latterly, the idea of relativity serve to the physicist. A. Hollard,[1] with much point, says:

"Cette hypothèse, comme toute hypothèse, a droit à notre crédit si elle est fructueuse au point de vue des faits qu'elle explique et qu'elle fait prévoir. Envisagée à ce point de vue, il est incontestable qu'elle a permis d'expliquer et de prévoir un nombre considérable de faits, entre lesquels on n'avait su discerner auparavant aucune espèce de relation. Que peut-on demander de plus à une hypothèse ? On ne saurait exiger qu'elle représente la forme définitive et invariable de la vérité. Tout au plus, une hypothèse peut-elle être une vue partielle de la vérité à laquelle, comme le dit très justement Dastre, l'esprit humain ne peut atteindre que par des approximations successives ? Au surplus, les hypothèses sont généralement provisoires et le plus souvent imparfaites ; leur principale raison d'être c'est leur utilité."

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[1] *La théorie des ions et l'electrolyse*, 1912, p. 4. (Gauthier-Villars, Paris.)

I. OHM'S LAW

This law and its applications are sufficiently familiar to all electrical engineers and students of science. Nothing more will be said of it.

II. FARADAY'S LAWS

Before stating Faraday's Laws in the modern text-book form, it will be both interesting and instructive to go to the fountainhead, and to consider for a moment how Faraday himself spoke of them. He tells us:

"In the first part of these researches, after proving the identity of electricities derived from different sources, and showing, by actual measurement, the extraordinary quantity of electricity evolved by a very feeble voltaic arrangement, I announced a law, derived from experiment, which seemed to me of the utmost importance to the science of electricity in general, and that branch of it denominated electro-chemistry in particular. The law was expressed thus: The chemical power of a current of electricity is in direct proportion to the absolute quantity of electricity which passes."

This he calls THE DOCTRINE OF DEFINITE ELECTRO-CHEMICAL ACTION: in the text-books it is often referred to as the "First Law." Further on, Faraday continues:

"Then, again, the substances into which these" (*i.e.* electrolytes) "divide, under the influence of the electric current, form an exceedingly important general class. They are combining bodies; are directly associated with the fundamental parts of the doctrine of chemical affinity; and have each a definite proportion, in which they are evolved during electrolytic action. I have proposed to call these bodies generally *ions*, or particularly *anions* and *cations*, according as they appear at the *anode* or *cathode*; and the numbers representing the proportions in which they are evolved *electro-chemical equivalents*. . . . Electro-chemical equivalents coincide, and are the same with ordinary chemical equivalents."[1]

This doctrine of ELECTRO-CHEMICAL EQUIVALENTS is, in text-books, often called the "Second Law."

Such is Faraday's way of expressing the two facts he discovered which connect electrical with chemical action. These facts, as stated in text-books, read somewhat as follows:

(1) A definite quantity of electricity (coulombs), when passed through an electrolyte, does a certain, fixed, maximum amount of chemical work. In the case of a solution of a metallic salt, a definite quantity of electricity, when passed through the solution between two electrodes of the same metal as that contained in the solution, can cause a fixed, maximum amount of the metal to be deposited at the cathode, and an equal amount to be dissolved at the anode. The maximum amount of metal deposited or dissolved, at the cathode or anode, respectively, is fixed by the quantity

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[1] *Experimental Researches in Electricity.* (Everyman's Library, published by J. M. Dent & Co.)

of current passed. Less may be deposited or dissolved; but more cannot be.

Thus we have:

$$\text{Metal}\left\{\begin{matrix}\text{deposited}\\\text{dissolved}\end{matrix}\right\} \propto \text{Quantity of Electricity.}$$

(2) Considering only solutions of salts of the metals, if the same quantity of electricity be passed through solutions of different metals, the amounts of the metals deposited (when the maximums are liberated) stand to one another in the ratios of the equivalent weights of the metals. Thus, suppose a quantity of electricity, Q, say, is passed through solutions of the metals A, B, C . . . (conveniently arranged in series). Then the maximum amounts of the metals obtainable may be expressed, *inter se*, thus:

$$\text{Wt}_A : \text{Wt}_B : \text{Wt}_C = (\text{Equiv. wt.})_A : (\text{Equiv. wt.})_B : (\text{Equiv. wt.})_C.$$

It is the same at the anodes:

$$\begin{gathered}(\text{Amt. dissolved})_A : (\text{Amt. dissolved})_B : (\text{Amt. dissolved})_C\\ = (\text{Equiv. wt.})_A : (\text{Equiv. wt.})_B : (\text{Equiv. wt.})_C.\end{gathered}$$

A real familiarity with Faraday's laws is of great importance in many ways in practice. Two instances may be given:

(i) *They assist the operator to maintain economic control.*

Expense is no great matter, perhaps, where only one or two small vats are at work. But where, as frequently occurs, the plating shop is large and a number of large vats are employed, the cost of power becomes of importance. It may, in certain cases, *e.g.* electro-galvanizing, determine whether the electrolytic process can be economically employed or not. In the case of the large shop, or where the process has to run near the economic limit or is competitive, as in refining, Faraday's laws assist in this way. One may imagine the operator to soliloquize: "My power bill for the quarter is heavy. Am I getting full value for the electricity used? Or is there a waste anywhere? Faraday's laws tell me that for my current-consumption I ought to receive in deposit (x) lb. of metal. Am I getting it?" It is simple for him to test for himself. If he puts together a small (say 3-gall.) bath, using solution from one or other of his vats, passes a certain current (measured on an ammeter in circuit) for a certain time, and weighs the cathode both before and after passing the current, he has all the data necessary for calculating, on the basis of Faraday's first law, whether he obtains what he ought to get for the quantity of electricity passed. And obviously, if experiment tells the operator that he is getting only three-quarters, say, of the amount of metal that ought to be deposited, then there is a waste of power somewhere, and his power and process are costing too much. This simple operation can be extended to each vat in turn.

In the cycle, motor, and also most other works where nickel-plating is done, there used to be a great waste of electricity. The nickel ammonium sulphate solution was almost universally employed. Now, the amount of nickel that can be deposited from this solution, under even the best workshop conditions, rarely exceeds 80 to 85 per cent. of the maximum; the remaining 20 to 15 per cent. of electricity that goes through the solution causes liberation of other substances than nickel (metal) at the cathode—substances which, as, for instance, hydrogen, may be harmful to the deposit as well as the cause of increased cost. It is clear that in large shops, containing fifty or so vats, consuming some three hundred or more watts per hour, the loss from the cause indicated became considerable.

It is not so easy to put Faraday's laws to experimental use on the anode side of a plating vat. For ordinary workshop purposes, it is, perhaps, better not to try to do so. It is preferable, in this case, to note whether one's general anode consumption corresponds to the electricity used, using Faraday's laws for this purpose. In another soliloquy the operator may say: "My anode bill over the six months is £x, and I have used (y) units of electricity; the anodes must (or should) have dissolved into the solution. Is this amount that which Faraday's laws tell me (y) units of electricity will dissolve in a solution working at maximum efficiency?"

(ii) *The evaluation of the working efficiency of a solution.*

The second instance that will be given of the employment of Faraday's laws in workshop practice for general control purposes concerns the installation for this or that purpose of new solutions, previously unknown as regards their working properties and value. When a new solution is proposed as a substitute for one already in use, the following matters (*inter alia*) should be considered:

(*a*) Will the deposit be, for the purposes required, a better one than that already obtained from the solution being used?

(*b*) Is the solution proposed easier to work and control?

(*c*) Will it be more economical?

(*d*) Will the deposit required be obtained more quickly? If the answer to this question is Yes, then the capacity or output of the shop will be increased.

Something will be said about (*a*) later: (*c*) and (*d*) are the considerations to which attention is drawn immediately.

One solution is less expensive than another to work if it is more efficient. It may also work more quickly because it is more efficient. The efficiency, as compared with the old solution, can clearly be determined by passing the same current for the same time through a small (3-gall.) vat of each—the old and the new solution, the vats being in series, and by weighing and comparing the weights of (1) the deposits and (2) the anode losses. If the new solution is to be tested (and it ought to be) in respect to whether it gives full value, at anode and cathode, for power consumption, then the procedure can, of course, be as given in (i). But suppose no sufficiently accurate low-reading ammeter is available. It does not matter, for, in this case, one can take advantage of a knowledge of Faraday's Law II. Thus: Place a small vat (3-gall.) of the new solution in series with a copper coulommeter.[1] Pass any appropriate quantity of current through the two, and weigh the deposits. Then we know that, according to Faraday's Law II., the following relation:

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[1] *Coulommeter* is the name now often given to what used, in general, to be called a voltameter. The name was, it is believed, proposed by F. M. Perkin.

$$\frac{\text{Dep. from new soln.}}{\text{Dep. from coulom.}} = \frac{\text{Equiv. wt. of metal in new soln.}}{\text{Equiv. wt. of copper (divalent)}} = X$$

should hold, if the new solution is giving full value. If the quotient on the left of the equation does not equal that on the right, then the deposit from the new solution falls short in amount from the maximum; and a simple calculation shows the amount by which it falls, and hence the percentage loss in the working of the solution.

If the anode side is considered, one has

$$\frac{\text{Loss of anode in new soln.}}{\text{Loss of anode in coulom.}} = X$$

It may be mentioned that such determinations as those indicated are usually referred to by electro-metallurgists as estimations of anode and cathode efficiencies, which are stated in percentages of the theoretical values. The calculations from the experimental data are matters of simple arithmetic: the necessary constants (electro-chemical equivalents, etc.) can be found in any good text-book on electro-metallurgy (*vide* list of References at the end of this chapter).

III. THE IONIC THEORY

Another name for this theory is the Theory of Electrolytic Dissociation: more occasionally it is referred to as "Arrhenius' Theory." The theory, though not due to Arrhenius, the Swedish physicist, received a great extension and development at his hands. In 1857, R. Clausius had already put forward the explanation that, to account for the phenomena accompanying the passage of electricity through electrolytes, it was necessary to suppose that some of the molecules of the dissolved substance were split up into components which carried the current through the solution. Thirty years later, 1887, Arrhenius, as the general result of a prolonged series of investigations, published conclusions to the effect that, not a few, as Clausius assumed, but the majority of the molecules were split up or dissociated. One cannot do better than refer to Prof. J. Walker's explanation of the position. Quoting Maxwell, he states:[1]

"'Now Clausius supposes that it is on the constituent molecules n their intervals of freedom that the electromotive force acts, deflecting hem slightly from the paths they would otherwise have followed, and ausing the positive constituents to travel, on the whole, more in the positive than in the negative direction, and the negative constituents more in the negative direction than in the positive. The electromotive orce, therefore, does not produce the disruptions and reunions of the molecules, but finding these disruptions and reunions already going on, it influences the motion of the constituents during their intervals of reedom.'"

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[1] *Introduction to Physical Chemistry*, 4th ed., 1907, p. 239. (Macmillan.)

Commenting upon this passage from Maxwell Walker proceeds:

"The constituent molecules referred to in the [illegible]re, of course, the positive and negative radicles of the dissolved salt, *i.e.* the kation and anion of which it is assumed to be composed. At any one time, then, we have, on the hypothesis of Clausius, some portion of the salt molecules split up into their constituent ions, which, with their electric charges, move towards the appropriate electrodes. It must be observed that this partial dissociation of the dissolved substance is the normal condition of the liquid, and exists whether there is an electric current passing through the solution or not. All that the electric forces do is to direct the dissociated charged products to the electrodes and there discharge them. Nothing has been said [illegible] to the proportion of the dissolved substance which is dissociated into ions. For the purpose of accounting for the validity of Ohm's law in electrolytic solutions, a very small proportion will suffice, provided that the small quantity is always regenerated by the action of the molecules without any interference of the electrical forces. In proportion as the free ions are removed from the solution at the electrodes, Clausius supposes them to be regenerated by the collisions of the undissociated molecules,[1] so that the process of conduction and electrolysis goes on. If we are to give the hypothesis definiteness and precision, however, we must take account of the relative quantities of the electrolyte in the dissociated and undissociated states. The manner of doing this was first pointed out by Arrhenius, and it is to his hypothesis of electrolytic dissociation that we must resort if we wish to explain quantitatively the phenomena exhibited by electrolytic solutions, whether during electrolysis or in their ordinary state.

"Arrhenius supposes substances which give solutions that conduct electricity freely[2] to be *almost entirely* split up into their constituent ions, while solutions which yield solutions of feeble conductivity[3] are supposed by him to be split up only to a very small extent. In fact, he proposes to measure the degree of dissociation of a substance by the conductivity of its solutions. On his hypothesis, only those molecules which are split up into their constituent ions play any part in the conduction of electricity, the undissociated molecules remaining idle. It is obvious, therefore, that the conductivity of any given solution depends on two factors—the number of ions in the solution, and the rate at which these ions move. To simplify matters, we will, in what follows, only consider univalent ions, *i.e.*, those derived from monacid bases, monobasic acids, and the salts which they form by mutual neutralization. Every ion derived from these substances has the same charge of electricity, *i.e.*, 1 faraday per gram-ion. Since each carrier of electricity has the same load, the quantity carried can depend only on the number of carriers and on the speed at which they move. Now, the rate at which the ions move may . . . be determined from the work of Hittorf and Kohlrausch."

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[1] Cf. the quotation from G. D. Hinrichs—given below.

[2] *E.g.* solutions of mineral acids, alkali bases and the inorganic salts of the metals.

[3] *E.g.* water, solutions of ammonia, boric acid and most organic salts.

But interesting though they are, these matters cannot be discussed in this chapter.

It will be seen that this extract from Professor Walker's book makes clear the distinction between Clausius' and Arrhenius'[1] views. Clausius supposed a few only, Arrhenius a great number, of the molecules of a dissolved substance (which, in solution, conducted electricity freely) to be dissociated into electrically charged bodies called ions. Of course, it is not to be assumed that the ions, once formed, retain a continually separate existence. On the bases of the Ionic and Kinetic theories, an aqueous, conducting solution may be looked upon as consisting of an immense number of particles comprised (1) of molecules of the constituents, and (2) of ions formed from the individual molecules: the whole of the particles are in motion, their velocity (average) depending chiefly upon the temperature that obtains. An ion that has, at one instant, a separate existence, may anywhere meet an oppositely charged ion, unite with it, and so form a complete, electrically neutral molecule, which, again, in time becomes split up into ions. But on the whole there will be, at any instant, a certain considerable proportion of separately existing ions—the proportion depending upon such factors as temperature, dilution, and so on.

On careful consideration the foregoing extract shows also the relation of Faraday's laws to the Ionic theory. The ions are electrically charged bodies: the charge on each is definite and fixed. That is what Faraday tells us. He pointed out the quantitative relation between matter in the dissolved state and the electric charge associated with it: 1 gram-equivalent (*i.e.* equivalent weight in grams) is associated with 1 faraday of electricity. Hence, 108 gms. of silver, 31·5 gms. of copper (divalent, as in the acid copper bath), 63 gms. of copper (monovalent, as in the cyanide bath), 32·5 gms. of zinc, 29·5 gms. of nickel or cobalt, and so on, are associated with 1 faraday of electricity. It is thus easily seen how it happens that the passage of a definite quantity of electricity through a solution results in the separation of a definite quantity of a metal at the cathode (provided, of course, the current is all carried by the *metal* ions), and, further, why the amounts of two metals liberated by the passage of the same quantity of electricity stand to each other in the ratio of the equivalent weights of the metals. It may be stated here that the absolute quantity of electricity associated with 1 gram of hydrogen (in the ionic state), that is, 1 gram-equivalent, is 96,500 coulombs, which is equal to $28,950 \times 10^{10}$ electrostatic units.[1]

The following pictorial representation will help one to visualize the phenomena:

MeAc is a molecule of, say, some salt.

Upon solution in water, we have, assuming the metal to be monovalent, on the Dissociation theory:

Me^{+} and Ac^{-};

if divalent, trivalent . . . we have

Me^{++} and Ac^{--} (or $Ac^{-} + Ac^{-} = 2\ Ac^{-}$). . . .

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[1] Cf. Arrhenius, *Theories of Chemistry*, 1907, p. 62. (Longmans.)

Upon passing the current, we have:

$$\mathrm{Me}^+ \ \xleftarrow{\text{Cathode}} \qquad\qquad \mathrm{Ac}^- \ \xrightarrow{\text{Anode}}$$

$$\mathrm{Me}^+ + \ominus = \underset{\text{(neutral, deposited)}}{\mathrm{Me}} \qquad\qquad \mathrm{Ac}^- - \ominus = \underset{\text{(neutral, liberated)}}{\mathrm{Ac}}$$

It is to be noted:

(i) That if Me (the metal) is not a metal like copper, zinc . . . but is sodium, potassium, aluminium . . . then, instead of being deposited (from aqueous solution) upon discharge, it reacts with the water of the solution; if it be hydrogen, as in acid solution, the hydrogen is liberated as a gas.

(ii) Ac (the "acid radical") is so chosen in plating solutions that, upon discharge, it unites with or dissolves the substance of the anode, and thus the solution becomes replenished with metal. And this, it is to be noted, is the very best way in which to replace metal deposited out at the cathode: it is far better than the addition of metallic salts.

THE MECHANISM OF IONIZATION

HINRICHS' VIEW

A question arising out of the foregoing considerations—a matter upon which something has already been said, but which cannot be considered in any detail—is the following: If the molecules (or many of them) of a dissolved salt are split up into ions, how does this come to be? As a starting-point of study the reader may, after noting Clausius' view (quoted above), be referred to a paper by G. D. Hinrichs, which appeared some years ago in the *Comptes Rendus*, but which seems to have attracted very little attention. The paper is entitled "La mécanique de l'ionisation par solution," and in it the author gives the results of his investigations upon "la mécanique de l'acte de solution." The general conclusions may be stated generally in Hinrichs' own words:

"Le frottement de molécules rotatoires de l'eau, isolant électrique, produira de l'électricité statique. Les deux électricités, positive et négative, sont produites en quantités exactement égales. Cette électricite ne pouvant s'échapper à travers l'eau isolante, les deux atomes de la molécule du sel en sont chargés: l'atome de sodium reçoit l'électron positif; l'atome de chlore, l'électron négatif. *Par cette acte* la combinaison chimique de ces deux atomes est dissociée, et les deux atomes, chacun chargé d'un électron, sont devenus des ions.[1] Si la solution est assez diluée, chaque molécule du sel est entourée d'un très grand nombre de molécules d'eau non conductrice; donc les ions produits seront bien isolés, et pourront se mouvoir assez librement sans perdre leur charge électrique. Mais, si par la solution de plus de sel, le nombre de molécules d'eau pour chaque molécule de sel est diminué, l'isolation moléculaire des ions diminuera aussi : c'est-à-dire, que le pour 100 des molécules en solution qui sera ionisé diminuera rapidement avec la concentration de la solution. Il n'aura ionisation complète qu'en solution très diluée.

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[1] This requires modifications in the light of present-day knowledge. See *The Electron Theory*, by E. Fournier d'Albe. 1906 (Longmans): and Chapter X., *post.*

"Voilà le fondement posé de la mécanique de l'ionisation par solution simple. La rotation des molécules du menstrue effectue la solution et l'ionisation en même temps. Donc l'hypothèse Arrhenius est devenue un théorème démontré de la mécanique moléculaire."

Without expressing any opinion upon Hinrichs' views, the present author cites them as containing much food for thought in regard to the question put above.

THE AID OF THE MICROSCOPE

On referring above to the points that should be borne in mind when considering the introduction of a new solution, it was mentioned that regard should be had to the value or serviceableness of the deposit with reference to the purposes which this has to serve. If the deposit has to serve as a protector to the underlying metal, as is the case with zinc (and sometimes with tin and nickel), it must not be porous. If, as often in the case of iron, the object of the deposition is to build up a worn or under-gauge part of some piece of mechanism, the deposit must be solid and homogeneous and without impurities; it must not contain cracks and fissures, and must adhere firmly to the base metal on which it is deposited. Similarly in other cases.

There is only one really satisfactory way of controlling the structure of deposits and, consequently, from this point of view, the deposition process. The one sound method is that of the examination of the structure of the deposited metal with the aid of the microscope. Unaided visual examination is quite insufficient. A deposit may look to have the qualities desired in it; but it will often be found wanting, when the microscope is employed. Such control is, of course, recognized nowadays as essential in metallurgical works: all (or, at any rate, most) important works contain their metallographical equipment. But little has been done, in practice, in connection with electro-deposited metals. However, things are improving. In Germany and America researches have for some few years past been proceeding with a view to determining the relation between structure of deposit and conditions of deposition. References to some publications containing results of such inquiries are given in Chapter XI. In this country very little work has been done in this field of research.

The general results so far obtained, and which have a practical bearing, may, perhaps, be summarized thus:

1. Here, as elsewhere, things are often other than they seem: an apparently good deposit may contain hidden defects.

2. The structure of deposits varies with the different factors of deposition, such as current density, composition and strength of the solution used, movement or agitation of the electrolyte, and so on.

3. The relation between type of structure and conditions of deposition seems, for any one particular metal and type of solution, to be fixed

PLATE I.

A corner of the plating shop of the Enfield Cycle Co., Ltd., Redditch.

(This photograph was taken and kindly supplied to the author especially for this book.)

Frontispiece]

PLATE II.

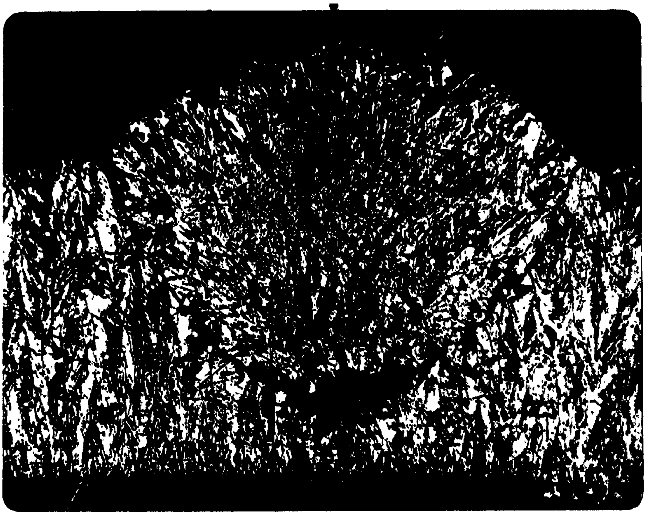

Fig. 1. × 170.

Showing the effect upon the structure caused by an inclusion of oxide.

PLATE III.

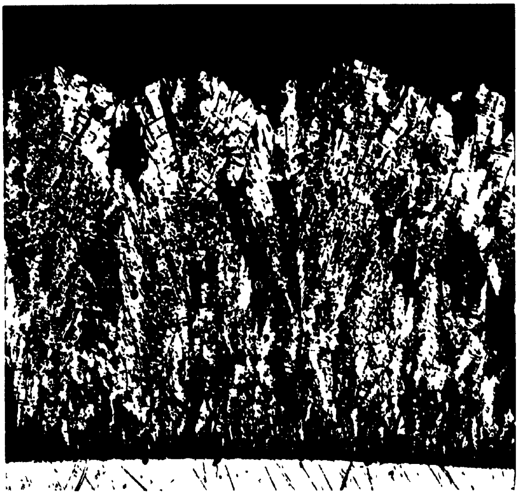

Fig. 2. × 160.

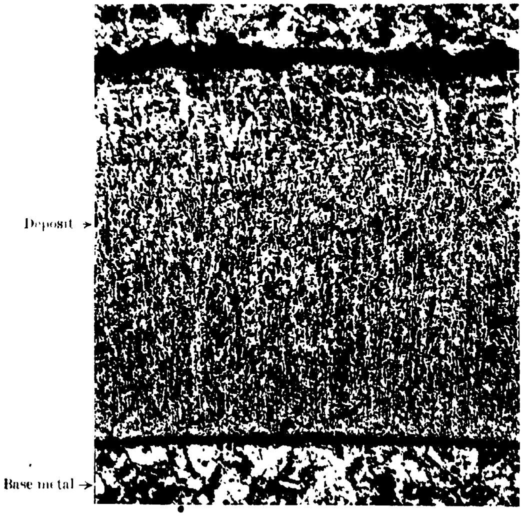

Fig. 3. × 160.

The photographs show the effect of the movement upon structure.
In Fig. 2 the cathode was stationary; in Fig. 3 it was moved.
Other conditions of deposition were, in all respects, the same.

PLATE IV.

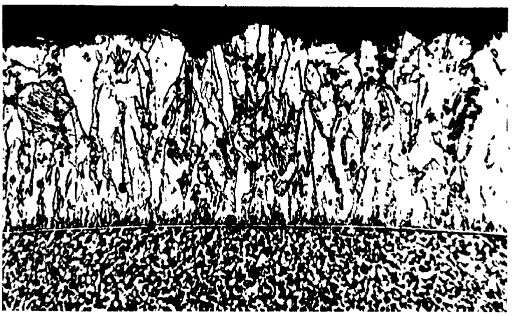

Fig. 4. × 100.

An iron deposit possessing normal structure.

Fig. 5. × 1500.

Structure of a deposit of nickel.

A high magnification is necessary in order to show up the structure well

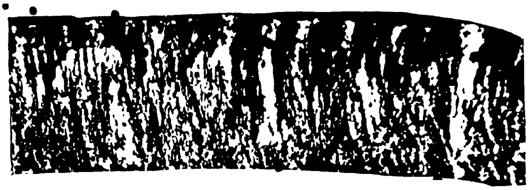

Fig. 6. × 40.

Fracture of a cobalt deposit.

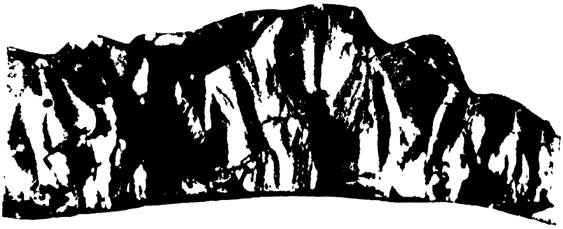

Fig. 7. × 40.

Fracture of an iron deposit.

so that if one knows the conditions which give a deposit having a certain structure, one can, by controlling the deposition conditions accordingly, obtain a deposit of the structure desired.

A few instances will now be given that will, it is suggested, show the utility of the aid of the microscope.[1]

Fig. 1 shows a polished and etched section of electro-deposited iron. The deposit looked sound enough when taken from the bath; but upon examination under the microscope was found to contain many such oxide inclusions as the one seen in the photograph.

Figs. 2 and 3 show the difference in structure between two deposits formed under all the same conditions of deposition, except that in the case of Fig. 2 the cathode receiving the deposit was stationary, whereas in that of Fig. 3 it was revolved. The photographs make clear how the structure is modified by agitation of the solution or movement of the cathode.

Fig. 4 is a photograph of a deposit of iron (magnified 100 times). This shows the normal structure possessed by an iron deposit when formed in a neutral solution.

Fig. 5 is a photograph of a nickel deposit formed in a solution containing a large amount of nickel (metal). The current density was 18 ampères per square foot. It will be noted how small the grain of the metal is.[2] This type of structure is obtained in the cases of copper, iron, or zinc, only when either special conditions of deposition are employed (as in the case of the deposit of Fig. 3, where the cathode was moved), or, often, where a considerable amount of free acid is employed.

Fig. 6 shows a fracture of a cobalt deposit. This is of special interest when compared with Fig. 7, which shows the fractured surface of an iron deposit. The deposit in the case of the iron is conchoidal, as the petrologist calls it; and, as has been pointed out by C. F. Burgess, this is a characteristic common both to many electro-deposits of iron and to certain minerals that occur in nature, such as hematite. Although somewhat similar to the iron, the fracture of the cobalt deposit is not so clean: this is notable in many cobalt deposits.

Very many other examples could be given; but sufficient have been shown to make clear how much can be learnt from an examination under the microscope of electro-deposited metal.

SUMMARY

The author has attempted to explain in the foregoing those natural laws which are the basis of all work on metal deposition; and an endeavour has been made to indicate how a knowledge of them, together with an understanding of the modern view of electrolysis, enables one to exercise informed control over the process of deposition. Such control can be extended and assured if the operator knows the conditions that give rise to this or that structure of deposit, or, in other words, has information which enables him to correlate deposition with structure.

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[1] Chapter XI., in which the structure of deposited metal is considered in some detail, will perhaps be of interest at this point.

[2] The magnification is: × 1500.

Perhaps this chapter may be fitly concluded with the sage advice of Le Blanc: "Ich habe bemüht, nach Möglichkeit allgemeinverständlich zu schreiben, möchte ich aber bemerken, dass für den, der mit geringen Vorkenntnissen an das Lesen . . . herantritt, ein ernstes Studium erforderlich ist, um rechten Nützen davon zu haben. Es gibt in der neuen Elektrochemie gewisse Anschauungsweisen, die sich ein jeder zu eigen machen muss, und dieses völlige Aneigen geht eben nicht ohne Arbeit." [1]

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[1] "In my writing I have striven to attain as great and general understanding as might be. Yet, I would like to remark that he who comes to the reading of this book with but little knowledge must necessarily devote to it earnest study, if he is to make good use of it. The ways of looking at things in the electro-chemistry of to-day require work for their mastery, if mastered they are to be." (*Lehrb. der Elektrochemie*, 1911, Preface).

CHAPTER III

PRACTICE: PREPARATION OF THE WORK

THIS chapter is intended to assist engineers especially. Its chief object is to sketch, in a general way, the practical operations of the workshop that have to be carried out in connection with the electrodeposition of metals, and, more particularly, in connection with electroplating. Some explanation of the scientific bases upon which the practical processes rest is given; a knowledge of and familiar acquaintance with the foundations is essential, if the work is to be conducted under proper control and with the greatest efficiency. As stated, the subject will be treated generally; details of the processes described, applicable in particular cases, will be reserved for the present.

The processes of practical electro-deposition may be classified under three headings: (1) Preparation of the work for the vat;[1] (2) the deposition process itself; and (3) "finishing" the work. The latter two operations will be treated in the next chapter

CLEANING

The whole success of the process of electro-deposition depends upon the manner in which the work is prepared for the vat. If the condition of the surface of the article is not clean, then the deposit will not adhere. By the word "clean" is meant not clean to the eye merely, but—really clean. For good adherence, the surface must be free from all grease, dirt, oxide ("scale" and rust), and liquids from vats through which the work has passed on its way to the plating tank. This essential condition precedent to good results cannot be too strongly or too often insisted upon.

In order to make quite clear how important the cleaning operations are, it will be useful, and also interesting, to consider, under a sub-heading, upon what factors the adherence of the deposit to the base metals depends.

THE ADHERENCE OF ELECTRO-DEPOSITS

Just exactly in what the adherence of a deposit to the base metal consists is unknown. Some authorities appear to think that there is formed at the junction, base metal—deposit, a thin layer of alloy consisting of the two.[1] If any such alloy is formed, it is beyond the limits of visual observation, even when this is aided by the highest powers of the microscope. The present writer has used magnifications up to 8000 diameters (obtained by the aid of a 2 mm. oil immersion, Zeiss apochromat objective), and yet failed to detect any appearance of the existence of an alloy. But such evidence, though negative, does not prove the non-existence of it; it is, however, such as to cause other reasons for the adherence of deposits to be looked for. Other authorities attribute the adherence to cohesion between the molecules (or atoms) of the base metal, and those of the deposit—cohesion of the kind that causes the molecules (or atoms) of a piece of any solid matter to hold together. It would seem that one or other of these causes must effect the adhesion of the deposited metal; perhaps both are operative. It is difficult to conceive any other cause. In any case it is clear that, unless the molecules (or atoms) of the base metal and the deposit can come within such close proximity to one another as to be within the range of action of the forces of alloying or cohesion, there can be no adhesion. And it is equally clear that, if something comes between the molecules (or atoms) of the base metal and those of the deposit, keeping the two apart, then the requisite proximity is not attained. Scale, rust, grease, oil, and the like, on the surface of the work, act as such partitions or, perhaps, one may say, isolators, and, consequently, where these are, there is not, nor can be, any kind of union between deposit and base metal. The intervening substance may be of another kind than those just cited. A typical example will help on this point. Suppose one wishes to deposit nickel or iron, and, for one purpose or another, it is considered necessary to deposit first a thin layer of copper on the iron before putting the work in the nickel-plating solution. (This, as a fact, is sometimes done, though in most cases it is quite unnecessary.) In order to "copper" the work, use must be made of the solution known as the cyanide of copper bath or, sometimes, as the "alkaline copper bath."[2] When the work has received its coat of copper in this, and is taken out, its surface is covered with the copper solution, and it must be swilled in water to remove this before being suspended in the nickel solution. But rinsing in water is not sufficient, if safety is to be assured. And for this reason: All metal is porous—some, of course, more than other; some of the cyanide solution has got into the pores, and it is not removed (at any rate, completely) by rinsing. The consequence is, that, when the work is put into the nickel bath, a chemical reaction takes place between the cyanide and the nickel solution, and a solid is separated as the result. This solid acts as separator between base metal and deposit, preventing the adhesion of the two.

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[1] In plating-shop parlance, the term "work" denotes the articles that are deposited upon. The word is very commonly indeed used with that signification; it is a short and convenient term, and will be used here.

The photo-micrographs, Figs. 8 and 9, show this. All the details of the preparation of the two articles for the reception of an iron deposit

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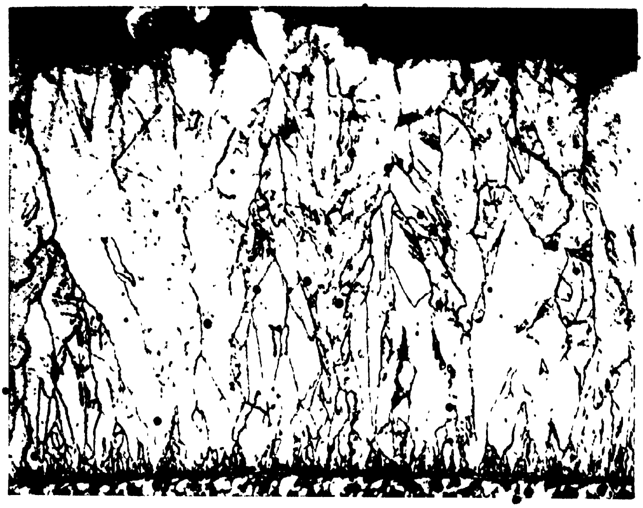
[1] C. H. Desch, "Report on Diffusion in Solids," *Brit. Assoc. Rep.*, Section 3, 1912; M. Schlötter, "Die Haftintensität und Legierung electrolytischer Metallniederschläge," *Chem. Ztg.*, 1914, vol. xxxviii. p. 289; G. Gore, *Electro-metallurgy*, 1906, p. 47; and F. Haber, *Trans. Amer. Electrochem. Soc.*, 1902, vol. ii. p. 189; see especially the discussion at the end of the paper, pp. 193–196.

[2] In contradistinction to the *acid* copper bath.

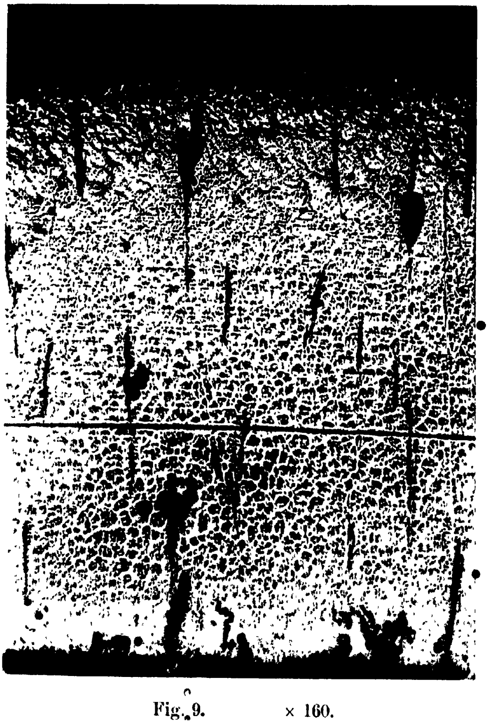
PLATE VI.



← Thin layer of copper between the steel base and the iron deposit

Fig. 8. × 200.

"Normal" structure of deposited iron. Compare the clean condition of the copper layer on which the deposit rests with the condition of the junction in Fig. 9.



← Hole caused by hydrogen gas

← A line of interruption due to complete stoppage of deposition

← Junction of base metal and deposit

Fig. 9. × 160.

The dual structure—fibrous and cellular—is interesting. Note the effect on the structure of gas evolution.

PLATE VII.

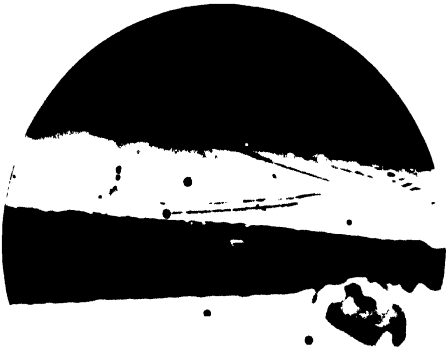


Fig. 10. × 1500.

The high magnification shows that the deposit must be very thin—at the part represented not much more than 0·001″ thick. This is typical of the nickel plating on cycle work.

Dirt on the surface of the seat-pillar, preventing adhesion of the deposit
Deposit

Fig. 11. × 1500.

The outer edge of the deposit, which was not more than 0·0015″ thick, is blurred in the photograph. This is due to "rounding" in the polishing process. The holes in the deposit are notable

were the same in the two cases, except that in the case of the article of Fig. 9 this was not swilled in an acid solution in order to "kill" the cyanide of copper that had got into the pores of the metal, or, perhaps, was not all removed from its surface in the water swill. As a result, the deposit did not everywhere adhere in this case. Figs. 10 and 11 are photo-micrographs that further and still more clearly illustrate the non-adherence of deposited metal that may occur through defective cleaning of the base metal. The photographs show different parts of one and the same polished section. The article was an ordinary bicycle seat-pillar, nickel-plated in the usual way in a works plating-shop. In Fig. 10 one sees how the deposit has come right away from the base metal—steel; while in Fig. 11 the cause is apparent. The dark band at the base of the deposit (or on the surface of the article) is material that prevents the adhesion of the deposit; it ought to have been removed in the cleaning process. Its presence is probably due to interaction between the potash, left on the surface after the article was swilled in water after removal from the potash cleaning tank, and preparatory to transfer to the plating bath, and the nickel solution.

METHODS OF CLEANING

These may be divided into: (1) Mechanical, (2) Chemical, and (3) Electro-chemical. Usually two of these methods must be employed in any given case—the mechanical and either the chemical or electro-chemical.

1. Mechanical Cleaning Processes

These are two in number. In the one, the article is scoured with Calais sand or pumice, a stiff bristle or, sometimes, an iron-wire brush being used; in the other, the work is sand-blasted. The former process (brushing with sand or pumice) is performed several times during the cleaning of the work; the latter is, in most cases, necessary only once. Both are simply mechanical in action, as is obvious.

2. Chemical Cleaning Processes

In these cases the action involved is chemical. It consists of the solution of the surface material by the chemical agent employed. For instance, representing rust[1] as an oxide, Fe_2O_3, the removal by hydrochloric acid is represented by:

$$Fe_2O_3 + 6HCl = 2FeCl_3 + 3H_2O.$$

Again, removal of grease by potash may be represented by:

$$\underset{\text{(ethereal salt)}}{(R'COO)_xR''} + \underset{\text{(potash)}}{xKOH} = \underset{\text{(metal salt)}}{xR'COOK} + \underset{\text{(glycerol)}}{R''(OH)_x}.$$

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[1] Rust is probably a much more complicated substance than is represented by this formula.

This represents the general case. But since the compositions (or "compos") used in the polishing shop are made of stearin (as a binder and lubricant) and some cutting or polishing material, such as kieselguhr (or tripoli), Vienna lime, or rouge (red oxide of iron), and it is the fat of these which has to be removed in the cleaning process, the particular case may be represented by:

$$\underset{\text{(stearin)}}{(C_{17}H_{35}COO)_3C_3H_5} + \underset{\text{(potash)}}{3KOH} = \underset{\text{(potassium stearate)}}{3C_{17}H_{35}\,COOK} + \underset{\text{(glycerol)}}{C_3H_5(OH)_3}$$

It may be remarked that the process here represented is known to chemists as "saponification."

It is important to bear these chemical equations in mind. They represent, typically, as has been said, the chemical actions that effect the removal of the material on the surface of the work. It is evident from them that a given amount of the chemical agent employed (acid, potash, and the like) will do only a certain amount of chemical work. When that much is done, there is no longer any of the agent left to do work; and, moreover, before it is all exhausted it may be too dilute (weak) properly to effect the desired result, since it is a well-known law of chemical action that the rate of this is proportional to the concentrations of the chemical agents acting.[1] The importance of this, from the practical point of view, is that it is of no use to continue using an acid dip or a potash solution that is not maintained at a suitable working strength. This is a matter that is sometimes neglected or lost sight of; it is one that will have to be further referred to.

3. Electro-Chemical Cleaning Processes

Such processes may be applied to the removal of scale, rust, or grease.[2] It is proposed to consider, first, the action whereby the surface material is removed, and then to discuss, scientifically, the advisability of the use of electro-chemical cleaning methods.

(a) *The Action of the Electro-Cleaning Process*

It is necessary, at the outset, to state briefly that the process consists in removing by means of the electric current such materials as exist on the surface of the work. The method of doing so is as follows: The work is suspended from the anode or cathode rod of a vat, put together in all respects as a plating tank, but having as liquid content a solution of some chemical, such as an acid, or cyanide, or potash, which, in solution, is a good conductor of electricity. Whether the solution is an acid or an alkali depends upon the work required to be done. Removal of scale and *thick* rust is effected in an acid solution; for removal of a thin layer of rust, or of grease, and, sometimes, of tarnish, an alkaline solution is used. A heavy current is then passed through the solution. In considering the way in which surface material is removed from the work, it will be convenient to take the case of grease, oil, and the like, first, and then consider the case of other substances.

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[1] This is known in Physical Chemistry as the Law of Mass Action. See J. W. Mellor, *Chemical Statics and Dynamics*, 1904, chaps. i. and ii.

[2] Details of various cleaning solutions (including the electro-chemical) will be given later.

The manner in which grease is removed from the surface of the articles to be cleaned has been carefully studied by Dr. A. Barth.[1] Upon the results of his experimental work Barth remarks as follows: "The extremely quick and thorough working of electrolytic de-greasing has hitherto been quite generally considered to be a purely chemical process, that is, as a saponification of the fatty matter by the caustic alkali which is formed, through the agency of the current, from the primarily separated alkali metal with liberation of hydrogen, and which is particularly active at the moment of its formation" (or, as the chemist would say, "in the nascent state"). "This theory is correct," continues Barth, "so far as the removal of saponifiable fatty matters is concerned. But it does not explain the lately established fact, that, in warmed de-greasing baths, machine oil, paraffin oil, and similar unsaponifiable matters are almost as quickly removed through the agency of the current as are easily saponifiable facts."

As regards such unsaponifiable matters, Barth concludes that the process of removal must be partly chemical and partly *mechanical*; and, to prove the truth of his conclusion, he made the following experiments: A moderately strong aqueous solution of alkaline carbonates was made, and it was heated to 85° to 100° Fahr. Pieces of polished iron sheet, having an area of two square decimetres, were thinly covered, some with ordinary fats, some with paraffin oil, and suspended in the solution from the cathode (negative) rod of the tank. A current was then passed, the pressure being 3 to 4 volts. It was found that whereas the sheets covered with fats were perfectly cleaned in two minutes, those with the oil upon them required a current strong enough to produce an *abundant* evolution of gas. Watching carefully the process of the gas evolution, Barth noticed that it occurred, first on the suspending wires, then on the edges and corners of the sheets (that is, where the oil layer was probably thinner and the current density certainly greater than in other places), and finally spread over the whole of the sheets. In the result the sheets were freed from the oil after the strong current had been passing some twelve to fifteen minutes, and could, after being swilled in water, be coated with an adherent coat of nickel. Barth noticed, too, that the higher the melting point of the substance used to smear the sheets and the lower the temperature of the solution was, the more difficult it was to clean the sheets. His conclusion is that the temperature of the solution must be sufficiently high to melt the substances to be removed from the work, as otherwise "the current cannot find the necessary points of attack, since it is not able to penetrate, and tear loose, layers of difficultly liquefiable fats. The removal of typically unsaponifiable liquid or melted substances in the de-greasing bath can only be explained by the purely mechanical operation of the bath, and this is effected as follows: By the action of the current, alkali metal is, in the first instance, deposited upon the base metal. The decomposition of water by the alkali metal which then occurs is accompanied by a sort of explosive evolution of very small gas bubbles which tear away the surrounding fat layer from the object. When one observes with what violence, particularly in hot electrolytes, the gas bubbles are repulsed from the surfaces of the objects, the mechanical tearing of the fatty layer becomes self-evident. It is, however, a root condition to the mechanical de-greasing by the gas bubbles that the alkali metal can become deposited between the object and the fat layer, which is only the case when the unsaponifiable layer is thinly fluid and easy to tear apart." Of the foregoing explanation given by Barth it may be said, that, if it is not the correct one, it is difficult to understand how else the unsaponifiable matters could be, as experience shows they undoubtedly are, removed from the surfaces of the articles by the electro-cleaning process.

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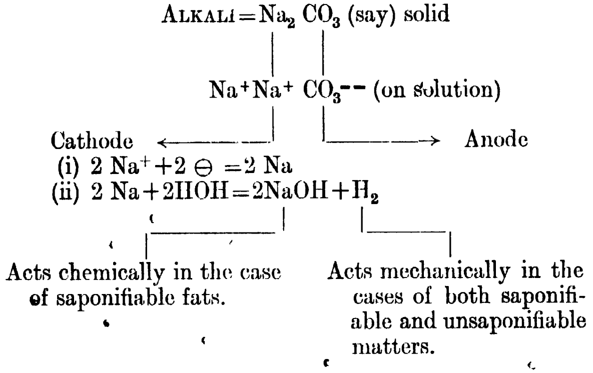
[1] *Chem. Ztg.*, 1911, p. 356.

Assuming Barth's explanation to be correct, then the mechanism of the process may be represented thus:[1]



ALKALI = $Na_2\ CO_3$ (say) solid

$Na^+ Na^+\ CO_3^{--}$ (on solution)

Cathode ← → Anode

(i) $2\ Na^+ + 2\ \ominus = 2\ Na$

(ii) $2\ Na + 2HOH = 2NaOH + H_2$

Acts chemically in the case of saponifiable fats.

Acts mechanically in the cases of both saponifiable and unsaponifiable matters.

Attention may now be directed to the use of the electro-cleaning process to remove other substances than grease, oil, and the like—substances such as scale, rust, and similar matters of an inorganic nature. The author has found that thin films of rust can be removed in a few moments in a solution of the composition used for de-greasing—an alkaline solution. The removal cannot, in this case, be due to saponification. It may, however, be due to reduction of the oxide (rust) by the nascent hydrogen; or it may be due to mechanical (scouring) action; or it may be due, perhaps, to both. The alkaline electro-cleaning solution is, however, of no use when thick layers of rust or fire-scale and the like substances have to be removed. The author has frequently used for this purpose a solution introduced by C. J. Reed,[2] and used it with great success. The bath recommended by Reed is simply a sulphuric acid solution of specific gravity 1·25; and the current density to be employed is 70 ampères per square foot of surface. He recommends that the temperature of the solution be maintained at 60° C., but the author has found this to be unnecessary; the bath works quite well at the ordinary temperature. In regard to the action of the removal of the scale, Reed says: "In the ordinary process" (of pickling) "the acid dissolves principally the metallic iron, and the scale is largely removed mechanically by the hydrogen gas formed under the scale. In the electric cathode process none of the scale is removed mechanically, as no gas is formed except by the current and none at all under the scale." This explanation is unsatisfactory. It is highly probable, indeed, that the removal of part of the scale is due to solvent action; but it is at least as likely that the removal is partly due to mechanical action similar to that operating in the de-greasing bath. If, in the first place, in the "ordinary process" hydrogen can act as a mechanical agent, *a fortiori*, one would suppose it so acts in the electric cleaner. Secondly, the present author, who has used the solution a great deal, and carefully observed the phenomena at the cathode during the action, has frequently noticed large quantities of, for the most part tiny, but sometimes comparatively large, pieces of scale being tossed about by the escaping gas in the neighbourhood of the work; moreover, scale can be sometimes seen to be torn off its surface. Thirdly, there is the analogy of the de-greasing bath, which Barth has carefully studied. No such careful work appears to have been done by Reed.

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[1] Equation (i) represents the action of discharge of the sodium ions, Na^+, Na^+; while equation (ii) represents the chemical reaction that occurs between the discharged sodium and water.

[2] *Trans. Am. Electrochem. Soc.*, 1907, vol. xi. p. 181.

(b) *Employment of the Electric Cleaner*

This or that process may be convenient and effective, but it does not necessarily follow that it is advisable to employ it. In regard to the electro-cleaning process, it may be said at once that it certainly ought *not* to be employed in the cases of certain classes of articles. No article that is to be subject to tensions or stresses should be subjected to the operation of electro-cleaning. Among such may be enumerated: springs of all kinds, cycle spokes, and, in general, articles that would be injuriously affected in working by loss of elasticity or flexibility. That the physical properties of metal that has been cleaned electrolytically are affected is now proved beyond doubt. It has been shown by M. De K. Thompson and C. N. Richardson,[1] and later by O. P. Watts and C. T. Fleckenstein,[2] that brittleness is undoubtedly produced in steel springs by electro-plating processes. There is no difference of opinion in these papers as to whether brittleness is produced; the only question was as to how the brittleness is caused—whether it is effected in some way by the free cyanide of the solution used or by the hydrogen electrolytically generated at the cathode (*i.e.* the article treated—the spring). Thompson and Richardson think the cyanide causes the brittleness; Watts and Fleckenstein show (and, in the opinion of the author conclusively show) that hydrogen is the cause. They show that brittleness is produced in cases where the solutions used contain no cyanide, such as sulphuric and hydrochloric acids, solutions of potassium sulphate and chloride, and also of caustic potash. Specifically, in regard to electro-cleaning baths they remark: "When used as cathode in the hot electric cleaner at 9 volts, and thus exposed to a storm of hydrogen, a spring is rendered quite brittle in fifteen seconds, and in thirty seconds is ruined."

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[1] *Met. and Chem. Eng.*, 1917, vol. xvi. p. 83.

[2] *Trans. Am. Electrochem. Soc.*, 1918, vol. xxxiii. p. 169. The author's attention has been particularly recalled to this paper by Prof. Watts in a personal communication.

The present author found that cycle spokes which were cleaned in a *cold* electro-cleaning solution, containing caustic potash and potassium cyanide, were rendered brittle.

It has been shown by J. Coulson[1] that the electro-pickeling process may affect the physical properties of iron and steel. But he found that while chemical and cathode pickeling produced embrittlement in steel springs, no brittleness was caused if the articles were pickled as anodes. It cannot, however, be sound practice to pickle work such as springs, spokes, and the like, as anodes. As C. Hering pointed out in the discussion on Coulson's paper, it is difficult to believe that they would not be attacked to a greater or less extent. The practice is wholly inadvisable. It must, at the same time, be pointed out that T. S. Fuller[2] has indicated a way whereby, he says, brittleness produced in steel springs by electro-plating may be prevented. He states that embrittlement is not caused by electro-plating if the articles are first dipped in molten tin, which (he says) does not appreciably affect the physical properties of the springs, even at a temperature of 260° to 300° C. Fuller believes that embrittlement is not caused under such conditions, because the nascent hydrogen cannot penetrate into the metal. The layer of tin on the dipped articles acts as a non-porous sheath. Presumably the same argument would apply to electro-pickeling or electro-cleaning; but the same process would, in many cases, be economically impossible, even if it were simple in action, which is doubtful.

The authorities cited and commented upon above, all make it clear that the electro-cleaning process must not be used on such work as springs, spokes, and similar articles; and most of them indicate as the reason that such articles are rendered brittle by the process, the brittleness being in some way or other brought about by the hydrogen "atmosphere" to which the articles are submitted. This is, indeed, but part of the larger subject of the occlusion of gases in metals and the effect of such occluded gases upon the physical properties of metals. It would not be in place to enter further into the subject here; but it is a very interesting and important one, and for that reason a reference to scientific publications on the matter is given at the end of Chapter IV. The author's immediate object is to point out and insist upon the care that must be exercised in regard to the use of electro-cleaning or electro-pickeling processes. Such care is especially important in the case of engineering work, since the articles to be dealt with are, in this case, usually made of iron and steel, which are particularly liable to be affected by gases, and especially by nascent gases. Apart from its use with articles of the kinds above mentioned, the electro-cleaning (or pickeling) process will, in many cases, be found to be both convenient and effective. Great care must, however, be taken to ensure the entire absence from the articles of the substances contained in the solution used, when the work is put into the plating tanks. (*Vide supra*, "The Adherence of Electro-deposits.")

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[1] *Trans. Am. Electrochem. Soc.*, 1917, vol. xxxii. p. 237.

[2] *Ibid.*, 1917, vol. xxxii. p. 245.

(c) *Examples of Cleaning*

A few examples will now be given to illustrate the actual process of freeing work that has to be plated from grease, oxide, and other surface material. The examples, which are actual cases that occur in daily practice, that will be considered are: (1) Cast-iron work, *e.g.*, sad-irons, air-bricks, and the like; (2) Cycle work; (3) Cast-iron printing rollers; and (4) Brass work, *e.g.*, cycle or motor lamps.

(1) *Cast-iron work.* This may be assumed to come to the depositor in the rough state in which it leaves the casting shop. It may be supposed that it has to be prepared for electro-galvanizing. Its surface is almost certainly covered, wholly or in places, with scale or oxide, which must be removed; and it has certainly been handled. The process of cleaning will be as follows: (i) Immerse in hot (boiling, if possible) potash, in order to remove any grease present on the surface and due to handling. (ii) Brush with a stiff bristle or iron-wire brush, using powdered pumice as abrasive in order to remove loose material (the work need not be swilled in water previous to brushing), and swill in clean, running water.[1] (iii) Pickle [2] in acid: this is aided by the previous removal of grease in the potash bath. The electro-pickeling solution may be used in this case with advantage. Brushing at intervals will help to remove loosened material. (iv) Remove from the pickeling solution after the surface has become freed from scale, and swill in water. (v) Brush as before, using pumice, and swill well in clean, running water.

(2) *Cycle work.* This usually comes into the plating shop in good condition. The surface has been polished in the polishing shop, and will have little or no oxide upon it. This fact simplifies the cleaning process, which will be as follows: (i) Remove grease in the potash solution. The electric cleaner may be used for certain of the work; this is a matter of discretion. (ii) Brush with pumice, and swill. (iii) Dip in very dilute sulphuric acid solution, in order to "kill" any potash remaining on the surface or in the pores of the metal, and swill. (iv) Brush again with pumice and swill thoroughly.

(3) *Printing rollers.* These are taken as examples of a type of work that frequently comes to the plating shop. Iron fenders polished on parts of the surface are other examples. They usually have a good surface free from scale or oxide. To clean them preparatory to, say, copper deposition: (i) Brush over the surface with hot potash solution, using a stiff bristle brush and pumice, and swill. If the work is of convenient form it can, of course, be immersed in hot potash. In any case the

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[1] It may be stated here, once for all, that all water used for rinsing purposes in the plating shop should be clean and fresh. A running stream of water should be maintained where possible.

[2] "To pickle" means to put into a solution that will remove scale, oxide, or sand. This term is generally used of acid solutions (or "dips," as they are called).

electric cleaner can be used if convenient. (ii) If potash is employed repeat the treatment, and swill thoroughly. The work is now ready for the plating tank. Acid dips are unnecessary, since the work must be given a coat of copper in the cyanide bath, which is alkaline, before being put in the acid copper solution in which the bulk of the copper will be deposited.

(4) *Brass work, e.g.*, cycle and motor lamps. This example of brass work is taken because it is somewhat more difficult to treat than work such as tubes or sheets, and the like. In assembling, the various parts, of which the lamps consist, are soldered together, and care must be taken that the solder suffers little or no attack by the solutions used in the cleaning process. The brass will be polished, and the polish must be destroyed as little as possible. The cleaning process may, therefore, be as follows: (i) Remove grease in the electric cleaner and swill.[1] This is preferable to the use of strong potash which attacks many solders. The work should not remain in the electric cleaner longer than is necessary, because, as stated above, caustic alkali is a product of the cathode reaction in the cleaner, and this will attack the solder in course of time. (ii) Brush with a soft bristle or fibre brush, using Calais sand[2] as an aid to the removal of any loose material. Calais sand must be used instead of pumice in this case, because it is important to preserve as far as possible the polish of the surface of the articles which they have when they come into the plating shop. To do so results in economy, since if the deposit—nickel, say—is formed on a roughened surface, the deposit will be at least as rough, if not more so, and the work will be more difficult to "finish" after being plated. (iii) Dip in dilute acid in order to destroy any alkaline material, swill, brush lightly and quickly, and finally swill thoroughly in clean, running water.

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[1] To swill is to rinse.

[2] In plating-shop parlance, "Brush with Calais sand" (or with pumice).

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CHAPTER V

PRACTICE (*continued*): THE DEPOSITION PROCESS AND THE FINISHING PROCESS

ONE of the most frequently occurring causes that stands in the way of the successful operation of a plating-solution is a want of knowledge on the part of the depositor of what a plating solution really consists. Sometimes the component substances contained in the bath are unknown, not only to the man who has to work the bath, but also to any one in authority in the works in which the bath is installed. The solution is made from salts already mixed before they come into the works, and the operator is left to get the best results he can by following written instructions sent with the salts. This is, and must always be, a most unsatisfactory position. The clearest and most carefully worded instructions are never sufficient to enable a man, however skilful a plater he may be, to work a solution of composition unknown to him at the maximum of efficiency and economy. If this fact is not obvious as soon as stated, no amount of labouring will make it clear.

But whether or not the contents of this or that particular solution are known to the man who has to work it or to supervise its working, there are certain principles upon which all good solutions have, perforce, to be based, and which should be borne in mind by all who have to do with those solutions.

ON SOLUTIONS IN GENERAL

1. The Component Substances of the Plating Solution

A solution from which metal is to be electro-deposited must contain a representative from one or more of the following classes of substances: (i) A salt containing the metal to be deposited; (ii) "Conducting salts" (so called), among which are included acids, which are often regarded by chemists as salts of hydrogen; and (iii) "Addition agents."

(i) *The metal-containing salts.* The salt of the metal used as a constituent of a plating solution is usually either the sulphate, *e.g.*, copper sulphate, zinc sulphate, iron sulphate, and so on, or the double cyanide, *e.g.*, silver potassium cyanide or copper potassium cyanide. Sometimes, though much less frequently, some other salt is employed. For instance, zinc chloride is used in some zinc baths; lead acetate is used in lead baths; and tartrates, fluosilicates, and other similarly uncommon substances are occasionally used. The sulphate is much to be preferred if it can be used, since it is usually cheaper, and one knows with greater certainty what takes place at the electrodes upon the electrolysis of a bath founded upon it, and hence one has a greater control over the working of the bath.

(ii) *Conducting salts.* These are usually salts of ammonia—the sulphate or the chloride, as, for instance, ammonium sulphate (often used in nickel baths) and ammonium chloride, which is used sometimes in both nickel and iron solutions. At times the sulphate or chloride of a metal of the alkali or alkaline earth group is employed. Sulphate of soda is added by Schlötter[1] to his iron bath; sodium chloride (common salt) is a frequent component of nickel baths; and calcium chloride is an essential constituent of the Fischer-Langbein iron depositing solution. Many other instances could be given. It may be remarked that potassium salts are but comparatively seldom used, the chief reason being that they are considerably more expensive than the corresponding sodium compounds. One reason for the use of "conducting salts" is, as the term implies, that they enable the current to pass more easily through the solution—they lessen the resistance. One result of this diminution of resistance is that the electromotive force required to pass any given current is (by Ohm's law) diminished also, and thus the cost of power for plating is lessened. Another result, equally as important, ensues. Suppose F is the anode-cathode potential drop. This E.M.F. is the algebraic sum of the potential between anode and solution on the one hand, and the potential between cathode and solution on the other. Thus, F=anode potential+cathode potential. If F diminishes, the sum of the anode and cathode potentials does so; and in most cases each of those components will share in the total diminution. It is the lessening of the potential at the cathode which is of most importance from the plating point of view. For the lower the cathode potential is, the less likely, *ceteris paribus*, is hydrogen to be liberated. Where hydrogen is liberated along with the metal to be deposited, two disadvantages result, namely: (1) The cathode efficiency, as regards metal, must be below 100 per cent., and the more hydrogen is liberated the lower the cathode efficiency will be (Faraday's law); and (2) the liberation of hydrogen has often an injurious effect upon the form in which the metal is deposited. It will be liable to be less coherent and to become powdery; the liberation of hydrogen in any considerable amount will cause the deposit to be useless. It will thus be seen that the cathode potential should always be kept as low as possible. One way of effecting this is to keep down the total anode-cathode potential, and the use of conducting salts is one way of doing this. The use of conducting salts is of advantage in other ways, though these are less generally apparent to those who work plating baths.[2] It will shorten the discussion to take an example. If a nickel bath is made that contains the sulphate only, of that metal, in solution, no reguline, useful deposit can be obtained. But if sulphate of ammonia be added (or if the salt known as nickel ammonium sulphate, or, in the plating shop, as "double nickel salts," be added), then the nickel is deposited out in the usual form. The function of the conducting salt (ammonium sulphate) is seen in the following chemical and electrochemical equations, which are taken from a paper of W. Pfanhauser, jun., who has worked out the reactions occurring at the electrodes during the operation of the double nickel sulphate bath.[1] The reactions at the cathode are the only ones of importance here.

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[1] *Vide* next chapter, p. 51.

[2] See A. Brochet, *Galvanoplastie*, 1908, at pp. 48, 49, and elsewhere; A Hollard, *La Théorie des Ions*, 1912, p. 200.

$$\mathrm{NiSO_4+(NH_4)_2SO_4=(NH_4)_2Ni(SO_4)_2} \quad \ldots\ldots\ldots \quad \text{(i)}$$

$$\mathrm{(NH_4)_2 \mid Ni(SO_4)_2} \quad \ldots\ldots\ldots \quad \text{(ii)}$$

$$\text{to cathode} \longleftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\longrightarrow \text{to anode} \quad \text{(iii)}$$

$$\mathrm{2(NH_4)+(NH_4)_2\,Ni(SO_4)_2=Ni+2(NH_4)_2SO_4} \quad \ldots \quad \text{(iv)}$$

$$\mathrm{2(NH_4)+2H_2O=2NH_4OH+H_2} \quad \ldots\ldots\ldots \quad \text{(v)}$$

One sees, therefore, that (i) the ammonium sulphate added to the nickel sulphate solution forms with this a double (or, rather, a complex) salt which (ii) splits up or ionizes into $(NH_4)_2$, as cation, and the complex, $Ni(SO_4)_2$, as anion; (iii) the cation travels to the cathode, and is discharged there; (iv) upon discharge, the (NH_4) reacts with double nickel salt in its neighbourhood; and replacing the nickel from this, gives rise to ammonium sulphate. The nickel is deposited on the cathode (the work, that is) as reguline metal. It will be noted, too, that some of the (NH_4) reacts with the water of the bath, and that hydrogen gas is formed. This occurrence helps one to understand why the cathode efficiency of the double nickel salt bath is so low; but it will be observed that the formation of hydrogen is the result of a secondary reaction, and does not result from discharge of hydrogen ions at the cathode. The hydrogen formed is, therefore, not so dangerous as it would be if it had the latter origin. The point of immediate importance here is, however, that the conducting salt has, in this case, another function than that of making the solution more conducting—assisting the passage of the current, that is. In this case it enables a reguline deposit to be obtained where, in its absence, one would not be formed; and it does this by causing the nickel to be deposited as the result of a *secondary* and purely chemical reaction instead of directly and immediately after discharge of the nickel ion. It is highly probable that nickel is not the only metal that can be so deposited. It used formerly to be thought that silver was deposited from the cyanide of potassium and silver in like manner: it is still believed[2] that copper is so deposited from the alkaline copper bath in which the copper is present as part of the complex anion, $Cu(CN)_2$. A paper published by F. Haber[3] has thrown some doubt upon the explanation being the right one in the case of silver, but it still holds, in general opinion, in that of copper.

(iii) *Addition agents.* This is the term by which a large number of substances are known in the electro-metallurgical world. Their function[1] is similar to the latter of the two functions of conducting salts just referred to: they, when present in the solution, frequently enable a deposit to be obtained from it when otherwise either no reguline deposit would be got at all or the grains of the deposit obtained would be non-coherent and the deposit would then be useless for practical purposes. A case in point is that of lead. No solution is known from which this metal can be deposited in coherent, small-grained form in the absence of some addition agent. Mr. F. C. Mathers has informed the writer that his well-known perchloric acid solution will not give satisfactory deposits of lead unless small amounts of peptone or olive oil (or one of some few other substances) are added to it.[2] It is the fact that, in the case of the metal zinc also, all the best baths used for depositing this metal (for what is called "electro-galvanizing," that is) contain a small amount of some addition agent which, in this case, is often gelatine or dextrin. The nature of the substance employed as addition agent has already been indicated. It is most frequently an organic substance, such as a gum or sugar, gum tragacanth, dextrose, and the like. Among other substances that have been employed are: naphthalene sulphonic acid, pyrogallol, resorcinal, glycerin, liquorice root and liquorice extract, eiconogen, and very many others. It is not always the case that the addition of an addition agent taken at random will produce the desired result: the particular substance to use in any particular case has to be found by trial. An addition agent which produces a good result in one case will (or may) be found to have injurious effects on the structure of the deposit in another. The fact is that very little is known about the way in which addition agents act. All that is certain is that they do act—either for good or for bad: and that when they do produce favourable results these are brought about alongside a diminution of the size of grains of which the deposit is formed, and these diminished grains adhere firmly together. It is thus useless to discuss the *modus operandi* of addition agents; but it will not be without some use to make some few remarks about their employment. In the first place it is notable that, in the great majority of cases, the amount of substance that must be added is very small. For instance, the quantity of gelatine that should be added to a copper sulphate or nickel ammonium sulphate solution in order to produce a bright and, so far as the eye can see, structureless deposit, amounts to a few (1 to 3) grams per gallon of solution. Secondly, addition agents are usually of colloidal nature or give rise to colloidal solutions. Aluminium sulphate—an inorganic compound—is often used in zinc baths.[3] It is known that the hydroxide which results from the hydrolysis of this salt can give rise to a colloidal solution. It may, therefore, very well be that the improvement of a deposit which often results from the presence of aluminium sulphate in the solution is connected with the presence of the colloidal substance. And, thirdly, no colloidal substance or one that will give rise to the presence of colloidal matter should ever be added to any solution unless the result it is going to have upon the deposit is definitely known beforehand for the particular case.

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[1] *Zeit. f. Elektrochemie*, 1901, vol. vii. p. 698.

[2] E. Spitzer, *Zeit. f. Elektrochemie*, 1905, vol. xi. p. 345; Brochet, *op. cit.*, p. 74; and *vide post*, p. 112 *et seq.*

[3] *Zeit. f. Elektrochemie*, 1904, vol. x. pp. 433 and 773; and see H. Danneel, *Zeit. f. Elektrochemie*, 1903, vol. ix. p. 763.

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[1] Cf. E. F. Kern, "The Function of Addition Agents in Electrolytes," *Trans. Am. Electrochem. Soc.*, 1909, vol. xv. p. 441.

[2] See F. C. Mathers and O. R. Overman, *Trans. Am. Electrochem. Soc.*, 1912, vol. xxi. p. 313.

[3] Cf. W. D. Bancroft, *Trans. Am. Electrochem. Soc.*, 1912, vol. xxi.; and M. Schlötter, *Galvanostegie*, Teil 1, pp. 38 and 51.

2. THE COMPOSITION OF THE SOLUTION SHOULD BE SIMPLE

The simpler the composition of a plating solution is, the more easy it will be to work and control. It is only rarely that a solution cannot be devised that contains only three components at most. As regards the conducting salt employed (where one is used), this should, if possible, contain the same acid radical as does the salt containing the metal. Thus, sulphuric acid, and not nitric acid, should be used in the acid copper bath; ammonium sulphate, and not the chloride, is used, as a rule, in the nickel sulphate bath; and so on. The result of observing this rule is that the number of different anions discharged at the anode is lessened; consequently, the knowledge of what is happening at the anode is more certain, and a better control can be maintained over the general working of the bath. A solution that contains half a dozen components will almost surely give the operator a lot of trouble, and it may easily become impossible to work satisfactorily at all.

3. THE ANODE AND CATHODE EFFICIENCIES

In all really good solutions these will be approximately 100 per cent. Usually the anode efficiency is lower than that at the cathode, and this means that metal is taken out of the solution faster than it is supplied to it. It means, too, that the bath will gradually become poor in metal, and this must be supplied from outside (*e.g.*, by addition of metal salts)—which is objectionable.

4. THE GENERAL CHARACTERS OF DEPOSITS

A good solution should give a deposit that possesses certain characteristics. The deposit should be close-grained: it should be matt and non-crystalline in appearance. It should be light in colour; but it ought not to be bright. A bright deposit is almost always hard and brittle. The bath should be capable of continuously yielding a deposit having the required qualities over a considerable length of time, that is to say, for three or four hours at least. A competent plater knows that his deposit is a good one if it is of good colour, smooth, dull, and non-crystalline (to the eye), and *if any outgrowth that forms on the edges of the articles is rounded in appearance.* Another characteristic of a good solution is that it will give a result that is of approximately the same thickness all over the surface of the articles. Owing to the way in which the current is distributed over the surface of a cathode, the thickness of the deposit will never be everywhere the same.[1] The deposit on re-entrant parts of the surface will, usually, be least, and that on corners and edges most. The lines of force between an anode and a cathode are distributed in exactly the same way as they would be between two metal conductors in air, or as they are in a magnetic field. Consequently, the current density will always vary over the area of a cathode (or anode), and since thickness of deposit varies with the current density, that thickness will not be uniform. Nevertheless, in all good solutions the conductivity will be good, and hence the thickness will not vary considerably—within the limits of total thickness required for ordinary plating purposes.[1]

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[1] See W. Pfanhauser, jun., *Zeit. f. Elektrochem.*, 1901, vol. vii. p. 895; or A. Brochet, *op. cit.*, p. 162. An interesting paper on this matter by K. Arndt and O. Clemens, *Chem. Ztg.*, 1922, vol. xlvi. p. 295, has recently been published.

ON DEPOSITION IN PRACTICE

With the principles set out above in mind, the operator can control his solutions much more effectively than if he does not know them. There are, too, a number of practical rules which have to be observed by all who wish to obtain the best results and avoid troubles. These will now be discussed.

(*a*) *Cleanliness* should be made a fetish. Girls should not be allowed to wash up their platters in the water used in the scouring and swilling troughs, as the writer once saw being done in a Walsall shop. All rods and vat and anode connections should be cleaned at least daily. Meters must be cared for; and the wires of the resistance boards must not be overloaded. Any " burnt " wire should be replaced. Care should be taken that the anodes are alive. This can easily be done by holding one end of a thick, flexible, copper wire against the cathode rod while the anode is lightly scratched with the other end. If the anode (or anode suspending hook, where that is tested) is alive, there will be a spark. After the vat has been disconnected for purposes of cleaning, it must be seen to that it is properly connected up again, anode connection to anode rod, and cathode connection to cathode rod. Connecting the anode lead to the cathode rod has frequently been the cause of trouble and expense. There is an important point to be observed with regard to the wires used for suspending the work in the solutions. In the majority of cases copper wire should be used, and it should be of sufficient gauge to carry the necessary current without heating. The use of brass wire is no real economy: the use of thin wire may result in badly burnt fingers, especially when using the electric cleaner. Wire that has been used for suspending articles that have to be coated with tin or zinc can be used again after dissolving off the metal; nickel-plated copper wire has a market value.

(*b*) *Nothing* should ever be suspended in a solution unless the current is passing. In the case of some kinds of solution (nickel and iron, for instance), if the work is in the vat and no current is flowing, slight oxidation will occur, and any deposit formed on an oxidized surface is very liable to peel off—in plating-shop language, the deposit " strips." In the cases of other solutions, *e.g.*, cyanide baths (copper and silver), the metal of which the work consists—copper or German silver, say—will dissolve if no current flows. In one case within the writer's experience the deposit formed on safety razors was of a distinctly pink tinge, and the cause of this was found to be that the solution contained a considerable percentage of copper, dissolved, no doubt, from the brass of which the goods were made. The custom that obtains in some nickel-plating shops of loading a vat with work just before the dinner hour, and delaying to start the current until work recommences after dinner, is an entirely reprehensible one. All articles dropped into the solution should be at once removed: in the case of iron or steel goods this can be easily done by means of an electro-magnet.

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[1] On the structure of deposits the following may be usefully consulted: M. Schlötter, *op. cit.*, pp. 28–41; A. J. Allmand, *Applied Electrochemistry*, 1912, p. 124 (E. Arnold); and F. Förster, *Electrochemie wässeriger Lösungen*, 1922, p. 384.

(*c*) *Good*, sound anodes should always be employed—anodes consisting of cast metal rather than those made of rolled metal.[1] As a general rule, as many anodes should be used as can be conveniently suspended from the positive rods. There is no economy in using poor or an insufficient number of anodes. The current has to get into the solution by way of the anodes, and the bath should be able to get as much of its metal as possible from the anodes. It follows that anodes must be cleaned down to the solid metal every day, for if the surface is not clean it cannot be easily attacked and dissolved, and, moreover, if the anode surface has a layer of oxide or of decomposition products upon it, there will be there a layer of non-conducting material which will hinder the free passage of the current. At the same time it does not at all follow that an anode should consist of commercially pure metal. In America nickel anodes of a purity 90–92 per cent. are preferred to those of a higher purity. A well-known firm writes: "The trade here demands nickel anodes of two grades, viz., 90–92 per cent. purity, and those of 95–97 per cent. purity. The most popular grade is the 90–92 per cent.; we sell a very much larger quantity of this grade than of the 95–97 per cent." The reason for this is that the less pure anodes dissolve better than those that are more pure, and feed the solution with metal better. This results from the fact that the iron, carbon, and other like substances contained in the anodes as impurities, set up local actions with the nickel (they act with this like a number of little cells) and help in the solution of the anode. Chemically pure nickel would, if used as anodes, be likely to become "passive," and then would not dissolve at all. Such considerations do not, however, apply to anodes of copper, silver, zinc, or tin. The metal used in these cases should be the purest commercial material obtainable. Other points connected with the shape, size, and composition of anodes will be referred to later.[2]

(*d*) *The practice* of using two cathode rods within two anode rods (a four-rod vat, that is), is to be condemned. The result of so doing is that, when the vat is loaded there will be two rows of work between two rows of anodes. Thus, only one side of the work is opposed to the anodes; the other side will be screened by the articles composing the other row of work. Comparatively little current will find its way between the articles of the one row to the inside surfaces of those of the other, and, consequently, these will receive relatively little deposit. It is not always easy to convince the workman of this fact, and of the further fact that, where such a system is adopted, the work must be very unevenly plated.[1] A similar argument applies to the employment of a central anode rod with a cathode rod on either side of it—in a three-rod vat.

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[1] An interesting article upon "Anodes for Electro-plating" is contained in *The Electrochemical Industry*, 1903, vol. i. p. 347. It is written by the well-known authorities, C. F. Burgess and C. Hambuechen.

[2] Cf. Chapter VI., p. 64, and Chapter X., p. 120.

(*e*) *The upkeep of the solution.* The rules of practice regarding the maintenance of the solution are of the greatest importance. (i) *The specific gravity.* The specific gravity of a solution is not in and by itself a reliable guide to its composition, though many of those who have to work plating solutions appear to think that it is. An example—an extreme one, doubtless—will clear up this point. The silver-plating solution is very subject to attack by both the oxygen and carbon dioxide of the air; and very soon after a new solution has been made up it can be shown to contain oxidation products and carbonates. These continue to increase and, together with the products formed at the electrodes (namely, cyanates, formates, alkalis, and others), soon constitute a considerable portion of the solid matter in the solution. The specific gravity is, of course, dependent upon these to the extent of their presence; and hence the hydrometer reading must in no long time become misleading as to the composition of the bath. It indicates the *total* amount of solids in the solution. Certainly, in the cases of some baths, for example, many nickel and cobalt solutions and some zinc and iron baths, the hydrometer reading is more useful, especially in the cases of newly-made solutions or such as have not been in work for any long time. And again, if an analysis of a solution be made to the extent of determining the percentage of metal it contains, then from this knowledge, together with the specific gravity, one can learn a good deal as to the composition of the bath. For instance, suppose a zinc bath gives the following figures: Zn (metal)$=$W% and spec. grav.$=S_1$. One can easily calculate[2] that zinc sulphate (anhydrous) contains$=\chi$% zinc as metal, and hence, that the percentage of salt in a solution containing W% metal is W_2: the specific gravity of a solution containing W_2% anhydrous zinc sulphate is S_2, say,[3] while the value found by the hydrometer is S_1. We thus know that the difference between the two specific gravities is due to substances other than zinc salts, and can then begin to consider what it is due to. (ii) *Feeding the bath with metal.* The ideal way of maintaining the metal content of a bath is by solution of the anode. Replenishment from outside—by way of the addition of metal salts—should always be regarded as a makeshift; and a bath that requires to be fed much in this way can never be looked upon as a good one. Nevertheless, it is often found necessary to resort to this method in practice: the "double nickel salts" solution is a common case. Where feeding from outside has to be done, the following rules of practice should be observed: (*a*) Nothing solid should ever be added to the solution. The salts it is necessary to add should be dissolved up in solution taken from the vat, and the solution should be effected in an enamelled iron bath (provided with some means of heating). The solution so made should then be returned to the vat through a linen or canvas filter. (*b*) The amount of salts that need to be added should be definitely worked out and known beforehand. It is a very bad practice to add any arbitrary quantity, trusting to chance as to whether that amount will be right or wrong. Such slipshod methods militate against proper control of the working of a bath. And it is quite easy to determine how much salts a bath needs, thus: Remove 2 gallons of solution from the vat; ascertain by trial how much this quantity requires to yield a good deposit; measure up the solution to find how many gallons there are in the vat; a little arithmetic gives one the amount required. (*c*) When the salts have been added, results must not be looked for at once. There is a curious fact to be remembered in connection with plating baths. New or recently refreshed ones often fail to give of their best until a considerable amount of current has been passed through them. It is quite unknown why this is so, but it is a most important fact to be borne in mind, since failure to recognize it may lead to the ruin of a bath, in consequence of the addition of substances that are not needed or the addition of an excess of a substance that is. (*d*) When additions are made to a solution, this should be done overnight or at the week-end, and the solution should be well stirred up. In this way the solution will be of uniform composition throughout, and time will be allowed for solid (insoluble) matter to settle down before the bath is required for use again. (*e*) Everything said above in regard to the addition of salts applies with equal force to the addition of any other solid substance whatever. (*f*) Just as nothing should be added to a solution (whether it be working well or badly) in an indefinite quantity, so nothing should be added for an indefinite purpose. All experiments should be tried with a definite amount of solution (conveniently, 2 gallons) taken from the vat. Experimental work in the plating-shop should always be encouraged, but it should not be carried out on a solution as a whole. This rule is one which those in charge of plating solutions are apt to forget or disregard—often with serious results.

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[1] H. and R. S. Hutton in 1908 patented an "Improved electro-plating process comprising the subjection of the article to be plated . . . to a differential plating by arranging screens or their equivalent (which produce a vignetting effect of the plated material upon the article) between anode and cathode. . . ." Pat. No. 18246. The point of this reference will be obvious in connection with what is said on previous page in sub-paragraph (*d*).

[2] From the chemical formula.

[3] Obtained from tables to be found in text-books.

(*f*) *Agitation.* In the great majority of cases it is advisable to provide either for agitation of the solution or movement of the articles while deposition proceeds. The advantages to be gained thereby are (*inter alia*) as follows: (i) The liquid at the surface of the work will be continuously renewed. (ii) Such renewal will allow of the employment of a higher current density. (iii) Greater output will be obtained in consequence of faster work. (iv) The structure of the deposits will be more uniform, and the solution will be maintained more uniform in composition, and stratification, due to the formation of layers of liquid of different composition, will be prevented. The method adopted to agitate the solution or move the work is not very material, so long as it is not one that is violent enough to disturb the sludge at the bottom of the vat or to injure the articles as the result of impacts. Moving the cathode rods to and fro, slowly, and in a direction parallel to the length of the vat, is a good method to employ, and it is one that any competent engineer can devise the means (simple and effective) of operating.

(*g*) "*Drying out.*" This operation comes between the deposition process proper and the "finishing" of the work. When the deposition is concluded, the work is removed from the plating solution, and should be well swilled in clean, running water (cold), and then in hot (nearly boiling) water. After passing through the hot water swill, the work is either put aside to cool and complete drying, or the drying is completed by rubbing the work with hot sawdust—preferably box-wood sawdust. The process of "drying out" would not have been mentioned here if it were not that trouble may arise owing to defective workmanship. The trouble that may arise is often called "spotting out."[1] It is due to insufficient swilling and drying; articles made of cast metal are especially troublesome in this respect, and particularly so when they have been plated in the copper cyanide or brass solution. If the solution (cyanide) that has found its way into the pores of the metal is not got rid of during the "drying out" process, it will be sure to make its presence known sooner or later. Round spots appear on the surface of the deposit wherever this has a hole in it, and the liquid that oozes from the hole will corrode the deposit. Copper—or brass—plated work may be completely spoiled in consequence. In the case of nickel-plated work, such as cycle and motor goods, it is of importance to dry it well. If such work is packed (for dispatch abroad, say) before it is properly dry, it will in all probability be rusty before it arrives at its destination. The remedy for "spotting out" is, unfortunately, not the same in all cases. The following is a method adopted by the writer, and, in many cases, with considerable success. To take an example—it was necessary to deposit a heavy coat of brass on motor parts, some of which were castings that were made of very bad and porous metal. The plated goods were removed from the plating solution, and first treated as above described. They were then immersed in a hot solution of oxalic acid, containing about 6 oz. of the acid dissolved in 1 gallon of water. They were left immersed for half an hour, swilled in hot water, and then placed in a hot-air oven. In most cases this method was successful. The hot oxalic acid solution does not seem to attack either deposited brass or copper; but it does attack the cyanide in the pores of the metal, and destroys it. Hot solution of boracic or of acetic acids have been used for the same purpose; but boracic acid was found less efficient, and acetic acid was found to stain the deposited metals. Where the base metal upon which the deposit is formed is copper or brass, a dilute (5% by vol.) solution of pure sulphuric acid may be used: this solution must be used cold—not hot. Moreover, it must *never* be employed where the base metal is iron or steel.

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[1] See references at the end of this chapter.

THE "FINISHING" PROCESS

Electro-deposits are usually dull in aspect, and possess little or no metallic lustre. The process of producing the appearance which the goods have when they come on to the market is called "finishing."[1] This is effected by means of "mops" and "compos." A mop consists of a number of circular pieces of linen or calico, fastened together by a leather centre. Sometimes the layers are stitched together, sometimes they are open. Compos consist of (i) polishing material, for example, tripoli, lime, or rouge; and (ii) a binder, which may be stearin, wax, or other like material, and which also acts as a lubricant. Compos are usually put up in the form of bars, which are about half the size of an ordinary brick. To "finish" an article, the mop (of convenient diameter) is set on the threaded end of a spindle which can be rotated by means of a belt or motor, the bar of compo to be used is pressed against the rotating mop in order to supply this with the polishing material, and the deposit then polished. When the polish has been obtained, it is often advisable to bring up the "colour," as polishers say, by pressing a bar of Vienna lime or chalk against the rotating mop, and then lightly mopping the deposit again. This removes some of the grease, and gives a fresh appearance to the deposit. Several points are noteworthy in connection with "finishing." (i) The peripheral speed of the mop is important. This depends upon both the R.P.M. of the spindle and the diameter of the mop. The lower the speed, the longer an article will take to finish, and thus the lower the output will be. On the other hand, if the speed be too great, too much of the deposit will be removed, and a sufficiently thick deposit may become too thin. (ii) A compo containing an abrasive should not be used to finish soft metals. The result would be both poor "finish" and waste. Tripoli is an abrasive, and should not be employed with such metals as copper or brass. (iii) It is important that the melting point of the stearin used in the compo should not be too high; if it is, the mop will become clogged. The materials to use in any given case is really a matter of judgment. In the case of a nickel deposit, for instance, if the deposit is hard and rough, tripoli compo will have to be used, followed by lime (Vienna lime) compo, while a soft, smooth deposit can be "finished" with lime.

The process of "finishing" or, indeed, of polishing in general, has not, so far as the writer is aware, been subjected to scientific investigation. But the operation of polishing pieces of metal for subsequent etching and study of its structure has been very carefully studied by Sir G. T. Beilby.[2] Beilby has shown that in this case the operation of polishing produces an amorphous film on the surface of the metal. (Cf. Fig. 30, *post.*) Dr. Rosenhain says:[3] "Now when a surface is subjected to the action of a polishing disc fed with a suitable polishing powder, the flowing action becomes intensified and the abrasive or cutting action either ceases entirely or at all events becomes relatively unimportant. Thus the action of a true polishing process is entirely different from that of grinding, in that the polishing process merely causes the surface layer of metal to assume a temporary mobility so that it becomes free to assume the smooth surface typical of a liquid under the influence of surface tension. The polishing process gives this temporary mobility to the metal partly by the purely mechanical disturbance of the surface molecules, owing to the intimate contact which is established by means of the extremely finely-divided polishing powder. But where such mechanical action is chiefly relied on—*as it is in these cases, where polishing is done at very high speeds, as in ordinary* '*buffing*'—the result is what may be termed a 'burnishing' of the surface. The metal is simply smeared forcibly all over the surface, and although a brilliant appearance results, the attempt to use such a surface for metallographic work fails, because on etching, when the outer skin of metal is dissolved away in order to reveal the structure of the mass, the old irregularities make their presence felt to such an extent as to render the surface useless." These remarks of Dr. Rosenhain contain practically all that is known of the scientific foundations upon which the art of "finishing" or "buffing," as it is sometimes called, rests.

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[1] Or sometimes "buffing," or again, "mopping."

[2] *Proc. Roy. Soc.*, 1903, vol. lxxii.; 1905, vol. lxxvi.; 1907, vol. lxxix; and 1909, vol. lxxxii. Also *Trans. Far. Soc.*, 1904, and *Jour. Inst. Metals*, 1911, vol. vi. p. 2.

[3] *Study of Physical Metallurgy*, 1914, pp. 25 and 26 (Constable).

PRACTICAL NOTES

1. Dips (except the hydrofluoric acid one) must be contained in earthenware vessels, provided with covers. Hydrofluoric acid should be contained in a lead-lined vessel.
2. The "akey" should be made up from its components to suit the metal to be treated. It is to be remembered that the nitric acid is the active agent in "akey": the sulphuric acid acts as a diluent or moderator, as does the nitrogen of the atmosphere in relation to the action of the oxygen.
3. All dips and the electro-cleaner (or electro-pickle) should be placed and used in a well-ventilated place, and provision made to carry off fumes. Short circuits or sparking must be avoided as much as possible when working an electric cleaner (or pickle); the hydrogen evolved forms with the oxygen of the air an explosive mixture.
4. The solutions need not be of the precise strengths given in the Table. These are merely indicative and general. The actual strength to use depends upon the conditions, such as class of work, metal, and so on: it must be left largely to the discretion and experience of the operator. Similarly for the specific gravities of the acids employed.
5. At intervals during the removal of surface materials the work should be removed from the dip or cleaner, and scoured with pumice or sand. This removes loose material, and hastens matters.
6. Nothing should be suspended in the electro-cleaner (or pickle) unless the knife-switch in the circuit is "in." The insertion of the work

TABLE I

METHODS OF CLEANING WORK

MATERIAL TO BE REMOVED.	METHOD OF REMOVING IT.	
	Chemical.	Electro-Chemical.
1 SCALE (from iron).	"Pickle" in acid solution: (i) HCl...5 to 10% (by vol.)[1] Sp. gr. (of acid used) = 1·2. (ii) H_2SO_4...10% (by vol.) Sp. gr. (of acid used) = 1·84.	Use Reed's solution (*vide* text).
2. RUST (from iron).	Dip in acid solution. The same solutions as in case 1 may be used.	The ordinary electro-cleaner employed for removing grease will often be found useful for removing slight rust.
3. OXIDE or tarnish (from copper and brass).	Dip in: (i) Cyanide solution KCN...4 to 8 oz. 1 gal. or NaCN. (ii) What is called "akey," *i.e.*, a mixture of impure sulphuric and nitric acids, containing brown oxides of nitrogen.	
4. SAND.	"Pickle" in acid solution: (i) Solutions as in 1 may effect the removal. (ii) HF...5 parts acid and 95 water, contained in a lead-lined vessel.	
5. GREASE.	Boil in POTASH: use, if possible, AMERICAN BROWN POTASH: 4 to 12 oz./gal. The proper strength to use varies with the metal to be cleaned. Brass and copper require a weaker solution than iron and steel. Too strong a potash solution will stain brass or copper. Employ the solution at as nearly boiling as may be. *N.B.*—As far as possible, avoid the employment of all "substitutes" for potash. This substance is the best of all for removing grease and the like.	Use: (i) A solution containing KOH or NaOH)...4 oz. KCN (or NaCN)...3 oz. to a gallon of water. (ii) A strong current (of any value)—with the article to be cleaned as CATHODE. (iii) CARBON ANODES.[2] Sometimes the positive lead is connected to the tank which then becomes anode. This is bad practice, since iron anodes are soluble in alkaline solutions. (iv) Heavy cable leads to tank, and suspending wire of a gauge sufficient to carry the current without heating.

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[1] Both the H_2SO_4 and HCl should be free of arsenic. Cf. O. W. Storey, *Met. and Chem. Eng.*, 1913, vol. ix, p. 45. The effect of arsenic is to retard the action of the acid.

[2] Those made of hard Acheson graphite are the best to use. They can be obtained cut to any size required. A good size is 2 ft. × 9 in. × ½ in.

should complete the circuit. This prevents chemical attack on the article by the material contained in the solution—a very important matter in many cases.

REFERENCES

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ELECTRO-CLEANING

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PICKLING

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ELECTRO-STRIPPING

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ON OCCLUSION OF GASES

A General Discussion, *Trans. Far. Soc.*, 1919, vol. xiv. p. 173.

ON ELECTRODE EFFICIENCY

Dr. Wells.—*Brass World*, 1922, p. 234.

ON "SPOTTING OUT"

Vide *Brass World*, 1905, p. 350; 1907, p. 65; 1908, p. 409; 1909, pp. 17, 40, and 429; 1912, pp. 40, 268, 311, and 397.

ON POLISHING

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CHAPTER V

IRON

ONE effect of the stern necessities of war-time conditions was to stimulate and promote scientific investigation and research. The value of such inquiry was, perforce, recognized; and as a result, both pure and applied science have largely progressed. Among other branches of applied science to benefit is electro-metallurgy in general and electro-deposition in particular, and in this latter field the use of electrolytic iron and the application of the deposition process in the case of that metal have made marked extension and progress.

USES AND APPLICATIONS

The uses to which electrolytic iron and the electro-deposition process for iron have been and can be applied in engineering have been recently pointed out elsewhere[1] by the writer, and the general conditions upon which the future industrial progress depends have been summarized.[2] These will, therefore, be but briefly enumerated here. The chief uses to which electrolytic iron has been hitherto put are (1) its employment a the material for the manufacture of parts of electrical machines, an (2) its use as the raw material for investigations into the physical an chemical properties of pure iron.[3] The process of electro-depositin iron has been employed for the following purposes: (1) "Steel-facing," by which is meant the deposition of a thin layer of iron upon surface to be printed from. The purpose in this case is to impose a hard surfac layer upon the softer material of the printing block (which is often copper) and thus, by securing a better wearing surface, enable a much large number of true copies to be obtained. (2) The production of electrotype in substitution for those produced from copper. The process of depositio suitable for this work was worked out by M. H. von Jacobi and E. Klein, and it was extended and improved by S. Maximowitsch. It is interestin to recall that the following notice of this process appeared in the *Athenæu* published on May 4, 1869: "While M. Daguerre and Mr. Fox Talbo have been dipping their pencils in the solar spectrum, and astonishin us with their inventions" (which were connected with photography)

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[1] *The Engineer*, Oct. 8, 1920.

[2] *The Electrician*, Nov. 5, 1920.

[3] Vide *Bull. de l'Acad. Imper. des Sci. de St. Petersbourg*, 1869, vol. xiii. p. 40; *Bri Assoc. Rep.*, 1869, p. 67; W. Roberts-Austen, *Jour. Iron and Steel Inst.*, 1887, No. 1 p. 71; and S. Maximowitsch, *Zeit. f. Elektrochem.*, 1905, vol. ii. pp. 52 and 91. Cf. als F. Haber, *Zeit. f. Elektrochem.*, 1898, vol. iv. p. 410.

"it appears that Professor Jacobi, at St. Petersburg, has also made a discovery which promises to be of little less importance to the arts. He has found a method—if we understand our informant rightly—of converting any line, however fine, engraved on copper, into a relief by galvanic process. The Emperor of Russia has placed at the professor's disposal funds to enable him to complete his discovery." The process was used continuously at the Government printing-press in St. Petersburg from the time of its invention until—at any rate—the recent Russian revolution. It was also used at the Government press in Vienna. (3) For the following engineering purposes: The formation of "steel" driving bands on shells; the building up of worn and undergauge parts of aeroplanes; lining aeroplane engine cylinders; the formation of bushes on ball races and other parts; coating steel tubes; and many others, including the manufacture of sheets and tubes.[1]

A few remarks upon the above-mentioned uses and applications of electrolytic iron will be in place here. In the first place, it may be at once said that where the expression "steel" is used in connection with electro-deposited iron, the use of the word is unwarranted and apt to be misleading. Steel has never been electro-deposited; tentative trials have been made to that end, but only iron admixed with a percentage of carbon was obtained. Next, it may be remarked that the object the deposited metal has to subserve renders it necessary to study its properties closely; and, since these vary according to the conditions of deposition, the control of these is imperative. The object of the depositor should be to obtain iron possessing certain pre-determined properties, and he must not be content with merely the deposition of iron. And, thirdly, since the margin within which the process can be carried out economically is narrow, the question of cost must always be kept in mind, and the waste usually associated with electro-deposition processes rigidly avoided.

PROPERTIES

Electrolytic iron is, almost always, of a fine light grey colour. If it is dark in colour it will almost certainly possess properties, such as brittleness, for instance, which are, in nearly all cases, undesirable. The deposited metal may or may not be pure: it may contain hydrogen, carbon, sulphur, and other elements in greater or less extent. Further, it may be hard or soft, brittle or tough, sound or unsound as regards cracks and crevices, of uniform or various structure, both in one and the same sample, and from specimen to specimen. All those properties depend upon the conditions under which the iron is deposited: they have been considered by the writer elsewhere.[2] The thermal properties of the metal are of considerable importance to the engineer. Its crystallizing (or re-crystallizing) properties on heating have been carefully studied by Professor H. C. H. Carpenter and Dr. J. E. Stead.[3] These authors remark that the crystallizing properties of electrolytic iron are of great scientific interest, for in certain respects they are precisely the opposite of those of very mild steel and wrought iron. It may be added that these crystallizing properties are also of considerable importance. As typical of the difference referred to by Stead and Carpenter, the following comparison is given: "The very heat treatment that produces coarse crystals in the electro-deposited irons refines wrought iron and very mild steel that have been rendered coarsely crystalline by 'close-annealing' between 700° C. and 800° C. On the other hand, annealing at 700° C. to 800° C. has no effect in coarsening the structure of the electro-deposited iron which has been refined by cold mechanical work. In these respects, therefore, the behaviour of electro-deposited iron is precisely the opposite of that of wrought iron and mild steel. The re-crystallization phenomena of the pure electro-deposited iron can be most satisfactorily explained on the assumption that at Ar3 the iron changes direct from the γ to the α condition."[1] This matter of the peculiarities shown by electrolytic iron upon heat-treatment is of technical importance to the engineer, because it will be found to be often necessary to heat-treat the deposited metal after deposition if it is to be of real service for engineering purposes. It is, therefore, necessary to know what the effect of heat-treatment is, and how the result of such treatment compares with that obtained in the cases of other irons and steel. In connection with annealing, the recently published work of J. Cournot may be mentioned. As has been already stated, electrolytic iron may contain hydrogen; it will often be necessary to get rid of this impurity, for the presence of the gas in the metal may well give rise to a modification of its properties. Cournot has shown[2] that the time necessary for complete annealing varies with the temperature employed, if, indeed, one makes the assumptions he does that (1) the gas forms a hydride with the iron—a hydride easily disclosed by the microscope—and that the presence of this constituent is associated by an increase of hardness in the deposited metal. The present writer does not know of anything in the literature of electro-deposited iron that proves beyond doubt either that the included hydrogen forms a hydride with the iron or that hardness is the result of the inclusion of the gas; it is quite certain that the microscope does not disclose anything in the nature of a hydride. The writer is, therefore, not prepared to accept Cournot's assumptions as justifiable; but while that is so, Cournot's work shows that the annealing of electrolytic iron is not the simple matter it is usually supposed to be, and the hardness of the metal will vary with the length and temperature of the annealing to which it is subjected. Another property of electrolytic iron that may well be of great importance is its amenability to "case-hardening." This property has, up to the present, been but very casually studied, and no very reliable data are available. A paper by W. A. Macfadyen,[3] though not of much importance in other respects, contains some interesting and, it is believed, new observations with regard to the results obtained when electrolytic iron is case-hardened. He found that if iron was deposited upon a steel base,

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[1] L. Guillet, *Jour. Iron and Steel Inst.*, 1914, No. 2, p. 66.

[2] Vide *Jour. Iron and Steel Inst.*, 1920, No. 1, p. 321.

[3] *Jour. Iron and Steel Inst.*, 1913, No. 2, p. 119.

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[1] *Op. cit.* at pp. 144 and 145.

[2] *Compt. rend.*, 1920, vol. clxxi. p. 170.

[3] *Trans. Far. Soc.*, 1920, vol. xv. p. 98.

e.g., a steel tube, and the whole then annealed at a temperature above 900° C. for a short period, case-hardened at 800° C., and slowly cooled, the dividing line between deposit and base metal disappeared, and that there was no break in continuity between the two. Macfadyen's experiment is indicative only, it is true, and its indication is negative rather than positive. It shows that deposited iron can be subjected to "heating in a nitrogenous carburizing mixture" at the temperature stated, without harmful results occurring. He does not seem clear as to the objects to be obtained by case-hardening, and he gives no comparisons as between the Brinell or other hardness of the treated and untreated metal. Indeed, he previously states that heating at 950° C. for two hours is of itself sufficient to cause an interlocking of the grains of the deposited metal with those of the steel base. After such treatment "the dividing line was obliterated, its former position being marked by a wide, shady area between lighter deposit and darker basis metal." The important point to be noted is that, by the application of the ordinary heat-treatment processes, the sharp dividing line that always exists between deposit and base metal can be eliminated. The electrical and magnetic properties of electro-deposited iron cannot be discussed here: references will be found in the note [1] to some important literature on these properties.

ELECTRO-DEPOSITION OF IRON

The number of solutions (or baths) that have been proposed for the deposition of iron is very great. But the number of these that are of any real use is very small. With few exceptions, iron baths may be divided into two classes, namely, *Chloride* baths, or those based upon chlorides of iron, and *Sulphate* baths, or those based upon the sulphates. One of each class will be considered here: they both belong to the small number already referred to, and both have been put to practical workshop test.

I. The Ferrous Calcium Chloride Bath

This solution has proved itself of great worth in the workshop for depositing iron for a large number of purposes. It has been subjected to a thorough investigation by the writer.[2]

(*a*) *Composition and Electrode Reactions*

The ferrous calcium chloride bath is composed of:

Ferrous chloride, 450 gms. (16 oz.),
Calcium chloride (anhyd.), 500 gms. (18 oz.),

and

Water, 750 c.c. ($\frac{1}{6}$-gal.).

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[1] C. F. Burgess and A. H. Taylor, *Electrochem. and Met. Ind.*, 1906, vol. iv. p. 208; C. F. Burgess and J. Aston, *ibid.*, 1910, vol. viii. p. 191; L. Guillet, *Jour. Iron and Steel Inst.*, 1914, No. 2, p. 66; B. Neumann, Stahl. u. Eisen, 1914, vol. xxxiv. p. 1637; and C. Duisberg, *Internat. Cong. of App. Chem.*, 1912, vol. xxviii. p. 60. See also *Zeit. f. Elektrochem.*, 1909, vol. xv. p. 595.

[2] See W. E. Hughes, *Brass World*, 1922, vol. xviii. p. 261.

(i) *Composition.* Ferric chloride (ordinary perchloride of iron) may be substituted for the ferrous salt, if it is more convenient to use the former. But, in this case, it will be necessary to reduce the ferric iron to the ferrous condition, since solutions of ferric iron do not yield a deposit of metallic iron. This can be done thus: Add to the solution about ½-fl. oz. of pure hydrochloric acid to each gallon of the bath; suspend from the cathode rod as many and as large pieces of scrap iron as possible; and pass as much current as possible through the solution. The hydrogen gas liberated at the cathodes will reduce the ferric iron to the ferrous state. The passage of the current should be continued until a drop of the solution removed on a clean glass rod fails to produce a dark blue precipitate when introduced into a dilute solution of potassium ferrocyanide (yellow prussiate of potash) contained in a glass test-tube. The following substances may be used instead of calcium chloride, if it is more convenient: common salt, aluminium chloride, or magnesium chloride. The writer's experience is that common salt is quite a good substitute for the calcium salt; but, for preference, this should be used, if possible.

(ii) *Reactions.* It has been stated in a former chapter that the reactions occurring at the anode and cathode, while a bath is being electrolyzed, should be known as far as may be. By this means only can a really good control of the working of a solution be maintained. If the remarks made before be referred to or remembered, it will be seen that the double chloride of iron solution complies with the requisites of a good solution in this respect, namely, it is simple in composition. Nevertheless, it is the fact that the electrode reactions occurring during the electrolysis of the solution have never, so far as the writer is aware, been worked out scientifically. In the absence of strictly accurate data, one must, therefore, have recourse to the lessons and observations of practical experience. In the first place, it soon becomes evident from workshop experience that the anodes dissolve well; and, further, rough calculations have convinced the writer that, working at current densities round about 120 amp./ft.^{2}, the cathode efficiency is about 95 per cent. A current density of 20 amp./ft.^{2} can produce, as the maximum, a thickness of 0·001″ per hour from an iron (ferrous) solution. Time after time the writer has obtained, from the double chloride bath, a thickness of 0·005″ in one hour, working at 100 amp./ft.^{2} Next, bearing the foregoing facts in mind, one may be sure that the main reaction at the cathode is liberation of metal (iron). Some hydrogen is liberated, but the amount in weight must be very small. Looking to the anode side, the fact that the anodes dissolve so freely proves that the bath must be getting metal from them readily. The solution of the anodes is, no doubt, due to liberation of chlorine at their surfaces. The presence of chlorine in the anode region can easily be shown by chemical tests. Thus, simple observation shows that the main reactions of the bath are liberation of iron at the cathode and of chlorine at the anode. But it is not, in the absence of scientific proof, at all certain that these "end" reactions, as they may be called, are not the results—the algebraic sums, so to say—of other and more complex reactions. Indeed, there is very good reason for believing that they are; but to discuss the grounds for this statement would lead us far beyond the purpose of this book. If the "end" reactions be kept in mind, it will be sufficient, for control purposes, if these be considered to be the result of discharge of ferrous and chlorine ions at the cathode and anode respectively. The electrolytic rôle of the calcium chloride is thus undetermined; and it may for practical purposes remain so. One function of the calcium salt may, however, be noted, namely, that the addition of this substance prevents ready "alteration of the electrolyte at higher temperatures, whether by evaporation or oxidation."[1]

(b) *Conditions of Deposition*

The most suitable working conditions have shown themselves to be as follows: *Current density*, 90 to 120 amp./ft.^{2} This requires an E.M.F. of about 1 volt for an electrode distance of about 8″. *Temperature*, 90° to 110° C. *Anodes*, Swedish Iron anodes are the best to use. If sheet steel is used for anodes, a material as low in carbon as can be obtained should be employed, since the carbon, derived from the solution of the anodes, being exceedingly fine-grained, will float about in the solution and become incorporated to some extent in the deposit, forming an impurity in it. Carbon may give rise to other troubles also. It should, therefore, be avoided as far as possible.

(c) *Observations on Working Conditions*

One great advantage of the ferrous calcium chloride bath is that its working limits are wide. This fact goes far towards making the bath "fool-proof." It is advisable, in order to secure the best results, to keep fairly close to the conditions given above. The temperature must not be allowed to fall below 80° C., since at temperatures much below this the deposit obtained is unsatisfactory. The current density employed may be anything up to 200 amp./ft.^{2} A current density of this value will give an average thickness of deposit of between 0·009″ and 0·01″ per hour. Though this is so, yet it may be inadvisable to work at so fast a rate. The internal structure of the deposit depends upon the conditions that obtain during the deposition: the structure of a deposit obtained at 100 amp./ft.^{2} will be different from that of one formed at 200 amp./ft.^{2} Temperature is another factor that affects the structure of the deposit. The following sequence of changes occurs in the microscopic aspect of the deposit as the temperature rises from room temperature to above 90° C.: Very dark, bright, and hard, up to a temperature of about 35° C.; from this on, the deposit becomes lighter in colour, but remains bright and hard, then, as the temperature continues to rise, it becomes gradually more and more pale grey and less and less bright and hard; above 80° to 90° C., the deposit is light grey, matt or finely crystalline, and soft in aspect. It has to be remembered that macroscopic and microscopic features correspond generally; hence, there will be corresponding changes in the internal structure of the deposit as the temperature rises. It will, therefore, be seen that, although the difference of temperature, 90° to 110° C., and variations of current density of some few ampères per square foot about the mean current density 120 amp./ft.^{2}, will not make any great difference, the conditions given above should be approximately adhered to in general. Another working condition that is of considerable importance has not yet been referred to. Should movement be employed in the case of this bath? The advantages of movement (of solution or cathodes) have been pointed out for the general case in the previous chapter. The principal reason why movement should be employed in the case of the ferrous calcium chloride bath is connected with structure. If two deposits be formed under the conditions above given, and the current density and temperature are the same in both cases, then, if in the one case the cathode be moved during the deposition, the deposit in this case will be matt, while in the case of the other deposit (where there was no movement) it will be seen to be crystalline (cf. Fig. 2). Rod movement is the best kind to adopt in the case of this bath.

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[1] Eng. Pat. Nos. 24,841 (1909) and No. 25,969 (1910). For a discussion on the properties of iron deposited from the double chloride bath, see *Stahl u. Eisen*, 1912, pp. 801 to 805.

II. The Sulphate Bath

A great many baths founded upon sulphate of iron have been proposed. Each is considered to be the best by its "inventor." Many of them have been patented, though few would satisfy a Court of Law that they contained good subject-matter. The element of novelty is usually conspicuous by its absence. A knowledge of the requirements of a good solution for depositing metals enables one quite easily to build up a bath suitable for the deposition of iron from the sulphates. The bath proposed by Dr. Schlötter[1] may serve many purposes.

(a) *Composition and Electrode Reactions*

(i) *Composition.* Schlötter's solution contains:

"Acid" ferrous sulphate, 150 grms.
Sodium sulphate, 100 grms.
and
Water, 1 litre.

No light is thrown upon what is meant by *acid* ferrous sulphate by the chemical text-books. Any such special salt (if one exists) is not an ordinary article of commerce, and would certainly be expensive. It may safely be said that ordinary "green vitriol" can be used. The use of sodium sulphate may be advisable on several grounds. One of these is that it will perform the function of a "conducting salt"; another is that, at the concentration employed, the two salts may combine to form one salt which will give a complex anion containing metal (iron) as a component.[2] It is well known that solutions containing such complex anions often give better deposits than solutions containing only simple ions. The silver, copper cyanide, and nickel ammonium sulphate baths are examples. .The double salt of sodium and iron is, probably, more soluble than the double sulphate of iron and ammonium, and hence the solution can contain a higher metal content. None the less, it has been shown many times that where the solution is worked at a high temperature (as in Schlötter's) the ammonium salt serves quite well. And again, so long as the metal content is high, the precise amount of iron salt used is immaterial. Schlötter states that the bath is to be maintained slightly acid. Herein lies one of the difficulties of working sulphate baths. They must be kept slightly acid if the best results are to be obtained from them; but the acidity must be slight only, and the difficulty is to maintain the proper degree of acidity. As will be shown later, acid very markedly affects the structure of iron deposits; moreover, any considerable acidity causes liberation of hydrogen, and thus leads to lower cathode efficiency. The point of special note is that *any* sulphate bath made up on the lines of Schlötter's solution, one, that is, that is built up with the requisites of a good depositing solution in mind (high metal content, few kinds of ions, conductivity, and so on), will give good results.

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[1] Ger. Pat. No. 309,271 (1. 12. 17).

[2] On the subject of "complex ions," which the writer believes to play a considerable rôle in the reaction of depositing solutions, the reader will do well to consult R. A. Lehfeldt's *Electro-chemistry*, 1904, p. 133. (Longmans.)

(ii) *Reactions.* The same general remark that was made above with regard to the reactions of the ferrous chloride bath apply here also. No scientific work has been done upon it,[1] and, therefore, one has to use observations and experience for the purpose of exercising control. Here, too, there is but little hydrogen evolution at the cathode: the main reaction is separation of iron. At the anode the reaction is mainly solution of the iron or steel of which this consists, for there is very little evolution of gas (oxygen), and the anodes dissolve well. Some functions of the sodium sulphate have already been mentioned. If the bath is made slightly acid (this time with sulphuric acid), the anode efficiency will increase, but the cathode efficiency will decrease because more hydrogen will be evolved. A. Pfaff[2] maintains that the sulphate bath should have an acidity of 0·01N, if the deposition is to be long continued and the deposit is to remain smooth. The writer's experience is that much less acid is necessary, unless one wishes to secure unusually thick deposits—greater, that is to say, than some 0·01″ to 0·015″.

(*b*) *Conditions of Deposition*

It seems to be generally agreed that the sulphate bath must be worked at a raised temperature. C. F. Burgess and C. Hambuechen state[3] that they work at 30° C. A. Pfaff gives 70° C. as the temperature at which he obtained the best results. It is certain that if it is desired to use high current densities the temperature must be at least as high as 60° to 70° C. The writer has used the following conditions with success: *Temperature*, 70° to 80° C.; *Current density*, 100 amp./ft.^{2}; with this current density he has obtained deposits of sound and close-grained metal up to ⅛″ thick, and at the average rate of 4½-thousandths of an inch per hour; *Anodes*, Swedish iron.

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[1] On, that is, what may be called "double" sulphate baths. But cf. A. Russ and A. Bogomolny, *Zeit. f. Elektrochem.*, 1906, vol. xii. p. 697.

[2] *Zeit. f. Elektrochem.*, 1910, vol. xvi. p. 217.

[3] *Electrochem. Industry*, 1904, vol. ii. p. 184; *Trans. Am. Electrochem. Soc.*, 1904, vol. v. p. 201.

(c) *Observations on the Working Conditions*

The working limits of the sulphate bath are wide, except in regard to the important matter of free acid content. But the sulphate bath compares badly with the double chloride in these respects, namely, (1) the rate of oxidation of the solution is much greater (in the absence of considerable free acid), and (2) the rate of evaporation is greater also. The latter defect is especially harmful, since it is frequently necessary to add water to the solution, and this causes both a temperature drop and, more important still, the sludge at the bottom of the vat to be stirred up. For work on a large scale an automatic water feed has to be arranged. As regards the employment of movement, the remarks made above in regard to the chloride bath apply to the sulphate solution also.

GENERAL RULES OF PRACTICE

It is to be noted that the amount of a substance which can be held in solution at any temperature is limited. In general, the higher the temperature the more solid substance the solution can contain. It follows that a solution saturated at a higher temperature will deposit salts as the temperature cools. This is the case with hot iron baths, and is a source of inconvenience and, sometimes, of trouble. In order to prevent as far as possible the precipitation of salts, it is well to adopt some such procedure as the following: When work ceases at the end of the day, the heat supply, instead of being shut off, should be reduced only, the solution level having first been made up (if necessary) with *hot* water. At week-ends and before holidays such procedure would be too costly. In the case of the chloride baths there will be no difficulty in breaking up and re-dissolving the cake of salts which separates; but in the case of sulphate baths there will be more difficulty, since sulphates of iron are much less soluble than chlorides. In this case there is nothing else to be done except to maintain a small heat supply over the week-end or holiday, or to use a less-concentrated bath. This is a matter of cost and convenience, and has to be settled, in each case, in the light of working experience. A rule of practice which should be observed in the case of iron baths, and especially in the case of those that are maintained acid, is that the anodes should be removed from the solutions when work ceases; they should be well scoured and then dried. Another rule of practice, of general application, is one that should be observed very carefully in iron deposition. It is this: when once deposition has begun, the article receiving the deposit must not be removed from the solution, whether " to see how it is getting on," or for any other purpose. Every time that is done, the continuity of the deposit is broken: every such discontinuity can be seen on the polished and etched surface of the deposit. It is marked by a line (as seen in Fig. 12), and it may easily become the locus of fracture. For a similar reason the current must not be cut off during the deposition. And again, if movement is employed, this must be continued throughout the whole period: any stoppage of the movement can be seen if a polished and etched surface be examined (Fig. 13). There will be a change in structure, resulting from the change in conditions of deposition, namely, motion to no motion.

STRUCTURE OF IRON DEPOSITS

(*a*) *Macroscopic.* The appearance of a deposit should be light grey in colour, and it should be smooth. There should be little or no outgrowth at edges and corners. It should be either matt or very minutely crystalline to the naked eye: if it is bright and metallic, without visible structure, the deposit will be hard, but brittle. If the colour is dark and the deposit has, apparently, no structure, too much current has been used: excessive current is also proved by a powdery deposit, especially on corners and edges. Where an acid solution is employed, the deposit will be bright and hard-looking, but light grey if too much acid is present in the bath. If no means of movement is adopted, the macroscopic aspect will be, under normal conditions, crystalline, and the higher the current density employed, the more coarsely crystalline the deposit will appear. If movement is used, then, if the deposit looks crystalline to the eye, one can be pretty sure that the metal content is too low for the current density used: in this case, either more metal must be added or the current density lowered.

(*b*) *Microscopic.* As with all electro-deposits, so with deposited iron, macroscopic features and microscopic structures are correlated. A matt or bright deposit will be fibrous within: it will look as though it consists of thin threads or fibres. Acid and movement, each of them, will give rise to such an internal structure. If the deposit is crystalline to look at, the internal structure will be more or less coarse. It will consist, not of threads or fibres, but of grains which grow wider from within (near the base metal, that is) outwards. The more coarsely crystalline the deposit appears to the eye to be, the larger the grains of which it consists will be seen to be if a polished and etched section be examined under the microscope.

Figs. 2 and 3 (Chapter II.) make quite clear the difference between the fibrous and the so-called "normal" structures, the latter being that corresponding to a crystalline surface. Fig. 4 of the same chapter and Fig. 8 of Chapter III., also show the internal structure corresponding to a coarsely crystalline surface.

It is very clear from the illustrations in this chapter that a deposit that is fibrous throughout its thickness is more homogeneous in structure than any "normal" structure can be. Where homogeneity is required, precautions must be taken to adopt the deposition conditions that will produce it. At the same time it has to be remembered that a fibrous

PLATE VIII.

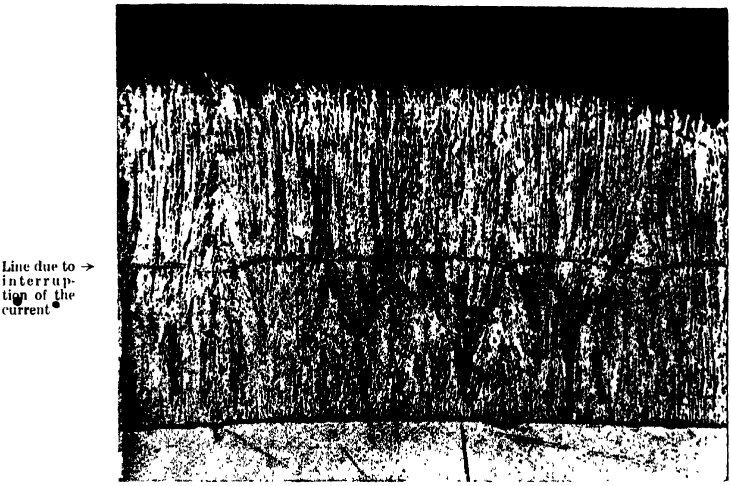

Fig. 12. × 160.

Deposit formed in sulphate of iron solution containing considerable free acid. The fibrous structure is very marked.

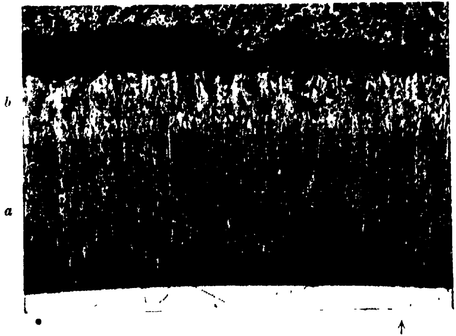

Fig. 13. × 100.

Deposit formed in chloride of iron solution. The change of structure from *a* (cathode moved) to *b* (cathode stationary) is clearly shown.

PLATE IX.

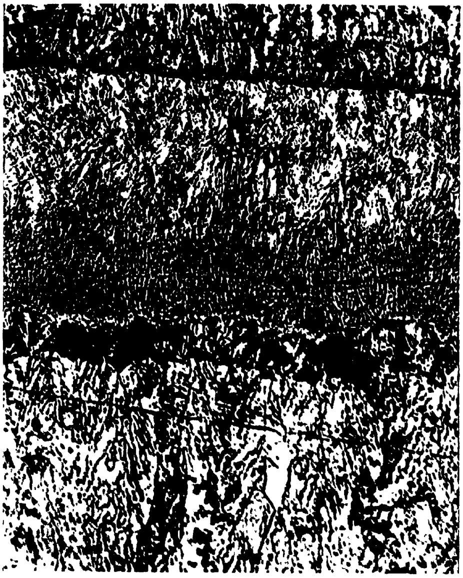

Fig. 14. × 200.

This deposit shows change of structure caused by introduction of acid into a neutral bath. At *a* the structure suddenly becomes fibrous, due to addition of acid.

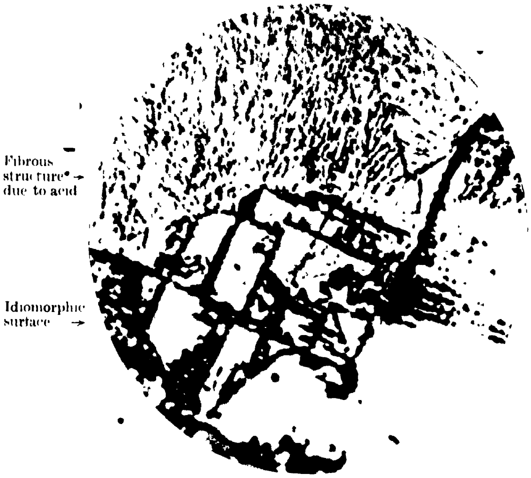

Fig. 15. × 1500.

The same deposit as shown in Fig. 14. Here the magnification is higher and the photograph shows the idiomorphic character of the surface of the deposit at the time when the acid was added.

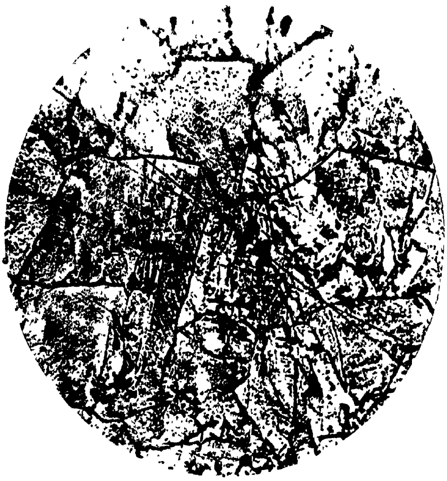

Fig. 16. × 400.

Hyp-idiomorphic structure of a deposit formed in the ferrous calcium chloride solution.

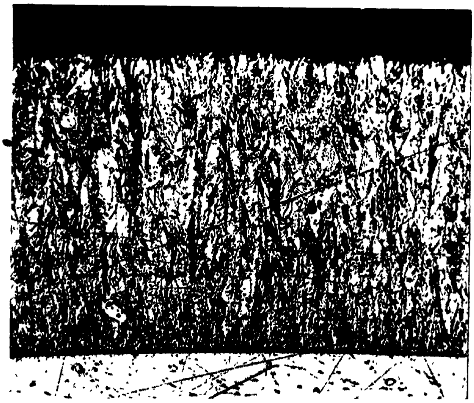

Fig. 17. × 150.

This deposit has a broken, but still "normal," structure. It was formed in a small quantity of solution (250 c.c.) and at high C.D. (120 amp./ft.^{2})

structure usually connotes brittleness, while a deposit that looks coarsely crystalline is nearly always more or less malleable. It has also to be observed that if a fibrous structure is being produced, and the conditions are changed during the deposition (if, for instance, movement is stopped, or, where acid is used to effect the fibrous form of structure, the acidity becomes too diminished) there will be a change in the structure. Thus, a deposit that is fibrous to begin with may change to one of normal type. Fig. 13 shows this change: it was due in this case to stoppage of movement. Figs. 14 and 15 illustrate the change—a very sudden one—from normal to fibrous, caused by the addition of an excess of acid to the bath.[1] Fig. 15, which is a micrograph of this deposit at higher magnification, shows that at the time the acid was introduced the surface of the deposit was covered with idiomorphic crystals of iron. Such a surface would have appeared to the naked eye very coarsely crystalline indeed—sparkling and brilliant from the light reflected from the facets of the crystals. The subscripts to Figs. 16 and 17 indicate sufficiently what they are intended to show. Fig. 17 is especially noteworthy.

A point that it is particularly wished to emphasize in connection with the illustrations of structure given, is that by the study of structure the depositor comes to obtain a very much greater control over the deposition process. A correlation of conditions of deposition and structure helps one to know of what a deposit really consists and, hence, to some extent, what its physical properties are.

REFERENCES

The author's *Electro-deposition of Iron* (published by H.M. Stationery Office) contains, as an Appendix, a list of all the more important work on Electrolytic Iron and its Deposition, published before about the middle of June 1921. Since that time the following papers have appeared:

GENERAL

F. A. EU[illegible]S.—"Economic Aspects and Possibilities of Electrolytic Iron."
This was a paper read before the *Amer. Min. and Metallurg. Soc.*, Sept. 1922.

B. STOUGHTON.—"Commercial Pure Iron and the 'Direct Process,'" *Chemical Age* (Amer. edit.), March 1922.

W. E. HUGHES, "Researches on the Electro-deposition of Iron," *Trans. Am. Electrochem. Soc.*, 1921, vol. xl. p. 185.
The discussion on this paper contains interesting information.

APPLICATIONS AND USES

B. STOUGHTON.—"Electrolytic Iron—a Commercial Product," *The Iron Age*, Jan. 5, 1922.

D. R. KELLOGG.—"Electrolytic Deposition of Iron as applied to Building up Worn and Under-sized Parts."
This is a paper read before the *Amer. Inst. of Min. and Metallurg. Eng.*

W. E. HUGHES.—"Building up Worn parts by Electro-deposition," *Chem. and Met. Eng.*, 1922, vol. xxvi. p. 267.

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[1] The writer has dealt more fully with the effect of acid in the structure of electro-deposited iron in a paper read at the ordinary meeting of the Faraday Society, 1922, vol. xvii. p. 442.

ELECTRO-DEPOSITION

H. D. HINELINE.—" Notes on the Electro-deposition of Iron," *Trans. Am. Electrochem. Soc.*, 1923.

This is an excellent paper on the practice of the deposition of Iron.

C. F. M'MAHON.—" The Manufacture of Electrolytic Iron," *Chem. and Met. Eng.*, 1922, vol. xxvi. p. 639.

F. A. EUSTIS and others.—" The Art of Making Electrolytic Iron," Amer. Pat. No. 1,412,174, April 11, 1922.

PROPERTIES

N. B. PILLING.—" Effect of Heat Treatment on the Hardness and Microstructure of Electrolytically-deposited Iron," *Trans. Am. Electrochem. Soc.*, 1922, vol. xlii. p. 9.

CHAPTER VI

NICKEL

THERE are two ideas, widely spread, in regard to the electro-deposition of nickel that are quite erroneous. The one is that the covering of an iron or steel article with a deposit of nickel prevents that article from rusting, and the other is that nickel cannot be electro-deposited in layers of more than a very few thousandths of an inch in thickness.

Nickel deposits in relation to rust prevention. The truth is that a nickel deposit will only prevent the subjacent iron (or steel) from rusting, if and so far as it prevents access to it by the atmosphere, that is to say, in so far as it forms a complete, non-porous covering over the iron.[1] If the layer of nickel is not complete (in the sense in which a coat of paint or varnish would be), then the nickel will, in fact, hasten the corrosion or rusting of the iron.[2] The reason is not far to seek: it may be expressed in the following way: When two different metals, in contact, are immersed in an electrolyte, the one will dissolve or oxidize faster than the other; the one that dissolves the faster protects, in a measure, the other. Electro-metallurgists say that the metal that dissolves the faster is electro-positive to the other: in Continental writings the former metal is called less "noble" than the latter. Now, a nickel-plated cycle crank, handle-bar, ammeter cover, or other article, may be regarded, when in use, as two pieces of different metal in contact and immersed in an electrolyte, namely, in this case, moist air, or, perhaps, more exactly, the aqueous vapour contained in the atmosphere. This contains—always—more or less carbonic acid gas dissolved in it: it may contain other gases, for example, carbon monoxide, sulphuretted hydrogen, or ozone, and it may contain sodium chloride and other like substances which, in solution, form strong electrolytes. In such an electrolyte the iron is electro-positive to the nickel; hence, the iron will dissolve where the moist air has access to it, and solution results in oxidation or rusting. Access of the air (and its contained moisture) to the iron (or steel) is not entirely prevented by the nickel deposit, for this is sufficiently porous to allow of it—at any rate when the layer of nickel is no thicker than that usually found on a nickel-plated article.[3] Moreover, very few articles of commerce that come into the plating shop present a perfectly plane, unbroken surface: cast metal, especially, is full of pits and holes, and even drawn and polished steel tube is not free from surface defects.

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[1] Vide *Brass World*, 1913, vol. ix. p. 382.

[2] Cf. M. Le Blanc, *Lehrbuch der Elektrochem.*, 1911, p. 176.

[3] Cf. Figs. 10 and 11, Chapter III.

Nickel solutions are notoriously poor conductors of electricity; consequently, but very little nickel is deposited upon the surfaces within the pits or holes, particularly when these are small in cross-section, but great in depth. Moisture and oxygen will gain access to the subjacent iron or steel by way of those holes, and rusting will result, and proceed faster, indeed, than if the nickel were not there.[1] It is clear, therefore, that nickel-plating does not *prevent* rusting or corrosion, except, indeed, where the underlying iron is completely covered, as, of course, it is, or may be, over some portions of the total area of the plated article. And hence the use of nickel-plating to serve that end can be only locally effective.

Thick nickel deposits. The idea that really thick deposits of nickel are difficult or impossible to obtain[2] has undoubtedly arisen from the fact that, in practice, a solution based upon the use of nickel ammonium sulphate,[3] as the metal-containing salt, is commonly employed. It is true that, from such a solution, it is difficult to obtain deposits of more than a few thousandths of an inch in thickness. Usually, after this is attained, the deposit strips or splits and peels off the base metal—the iron or steel. By taking great precautions thicker coats of nickel can be obtained; but, even then, the rate of formation of the deposit is slow, because where a solution contains nickel ammonium sulphate the current density employable is small, and, moreover, the cathode efficiency rarely reaches 90 per cent., and it is usually still lower in cases of continued deposition. If, however, a bath of the composition indicated below is employed[4]—one, that is, that contains no ammonia and, hence, no double nickel salts, there is no difficulty at all in obtaining deposits of nickel of, within reasonable limits, any desired thickness; and no special precautions and special manipulative skill are necessary to obtain them.

PROPERTIES

Electro-deposited nickel, like electro-deposited iron, varies in colour, hardness, and its other physical properties, from sample to sample. The properties possessed by any particular deposit depend upon both the composition of the solution and the conditions of deposition employed to form it. It may be brittle or malleable. In colour it may be light or dark, blue, grey, yellow, tin-white, and so on.[5] It is not true to say, as one writer does, that nickel has a silver-white lustre. It may be so hard that it is difficult to finish, or so soft that quite a high lustre can be produced on its surface by mere rubbing with the finger or a selvyt cloth. It is not easily oxidized or tarnished by the atmosphere, and it resists corrosion by other agents to a considerable degree. Indeed, its properties make deposited nickel very serviceable for decorative purposes, wherein lies the principal purpose of its wide application in practice. It may be mentioned here that the coating often referred to as "black nickel" is not nickel at all. It is an undetermined mixture of nickel and other substances—oxides and, perhaps, sulphides of that metal.[1]

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[1] Le Blanc, *loc. cit.*

[2] Cf. B. Blount, *Practical Electro-chemistry*, 1906, p. 113.

[3] This salt is known in the trade as "double nickel salts" or "double salts," simply.

[4] Namely, Solution 2. A paper on "Ductile Electrolytic Nickel," by C. P. Madsen, *Trans. Am. Electrochem. Soc.*, 1921, vol. xxxix. p. 483, contains much interesting information.

[5] Cf. E. Jordis, *Die Elektrolyse wässriger Metallsalzlösungen*, 1901, p. 60; and M. Schlötter, *Stahl u. Eisen*, 1921, vol. xli. p. 293.

THE DEPOSITION OF NICKEL

The reintroduction by Dr. Isaac Adams of nickel-plating solutions made of the double nickel salts or nickel ammonium sulphate was a great step in advance in the art of nickel deposition.[2] It is not true, as is sometimes alleged, that Adams originally suggested the use of double nickel salts. The credit for this is due to Dr. R. Böttger:[3] a nickel solution made from the double salts was employed under Roseleur's direction at a works in Grenelle, France, as early as 1849. Undoubtedly serviceable in their time, such solutions have, nevertheless, had their day, and their use at the present time is, for most purposes, bad practice. This view has also been expressed most emphatically by Prof. O. P. Watts[4] of Wisconsin University. The only further reference that will be made to the double sulphate type of solution (except, perhaps, *en passant*) will be to make a comparison between solutions of that type and baths of the type that should, nowadays, be installed in all up-to-date shops. This will be done at once, and, for the sake of convenience and brevity, be done by way of a tabulation (see Table II.).

In regard to the six matters in respect of which comparison is made in the Table, it may be said in general that—modern nickel baths, based on the "single salt" (or nickel sulphate), are: (1) Faster in work and, thus, give a greater output, saving space, it may be, thereby; and (2) more economical, because less troublesome to work—to keep in order, and to be made to yield satisfactory deposits. There is, too, less waste of power and material.

One further remark respecting the cathode efficiency of the double sulphate solution must be made. It has been claimed that this can be as high as 96 per cent.[5] But the solution used by the authors cited in Note 5 contained nickel chloride in addition to the double sulphate. Moreover, the deposition was conducted in the laboratory and under special conditions:[6] in this article the author is concerned with Works practice.

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[1] For the composition of "black nickelling" solutions and the method of working them, see J. Haas, *Metal Industry* (American edition), 1921, vol. xix. pp. 23 and 73; and for a more scientific investigation of the deposit, see K. Wetsch, *Diss. München*, 1910. See also G. B. Hogaboom and others, *Bur. Standards*, Tech. Paper No. 190.

[2] Amer. Pat. No. 93,157; and vide *Trans. Am. Electrochem. Soc.*, 1906, vol. ix. p. 211.

[3] *Jour. f. praktische Chemie*, vol. xxx. p. 267.

[4] "Some Observations on Nickel-plating Solutions," *Brass World*, 1915, vol. xi. p. 33.

[5] C. W. Bennett, H. C. Kenny and R. P. Dugliss, *Jour. Phys. Chem.*, 1914, vol. xviii. p. 373; *Trans. Am. Electrochem. Soc.*, 1914, vol. xxv. p. 335. Cf. also, for useful information, C. W. Bennett, C. C. Rose, and L. G. Tinkler, *Jour. Phys. Chem.*, 1915, vol. xix. p. 564.

[6] This remark applies also to the experiments of D. F. Calhane and Q. L. Gammage, *Jour. Am. Chem. Soc.*, 1907, vol. xxix. p. 1268, who, however, used a solution of the double salts only.

TABLE II

COMPARISON OF DOUBLE NICKEL SALTS AND MODERN NICKEL BATHS

	Double Nickel Salts Solution.	Modern Nickel Baths.
Metal Concentration	LOW. Not more than 8 to 12 oz. of the salts can be dissolved in 1 gal. of solution at the ordinary temperature.[1] As ammonium sulphate accumulates, the metal content becomes less, since the double salt becomes less and less soluble in it, and, consequently, is precipitated.[2] NICKEL AMMONIUM SULPHATE contains 14·87% Ni (metal).	HIGH. 3 or 4 lb. of metal salts can be easily retained in solution at the ordinary temperature.[1] NICKEL SULPHATE contains 20·9% Ni (metal).
C. D. Employable .	3 amp./ft.[2] (approx.) in a still bath.	The author has used as high a C.D. as 20 amp./ft.[2] during long-continued deposition in a *still* bath.
Cathode Efficiency .	LOW. Rarely as high as 90%; usually 70 to 80% in practice.[3]	HIGH. The author's determinations have shown that the cathode efficiency may attain 98%. Working with a 200-gal. bath, used in a plating shop, the efficiency was found to be 96·5%.
Anode Efficiency[4] .	LOW.	HIGH (comparatively).
CONTROL . . .	"The double nickel ammonium sulphate electrolytes must be carefully watched during operation to ensure satisfactory products, and the plater knows that his success depends upon keeping his solution at a chemical composition having somewhat narrow limits."—O.W. Brown, *op. cit.*	EASY (comparatively). The anode and cathode reactions are simpler, and troubles arising from alkalinity do not occur. (*Vide infra*, "Defects of Nickel-plating.")
Deposit . . .	Very often hard and difficult to finish. Often a bad colour—dark or yellow. More liable to pitting and peeling. Only thin deposits easily obtained. Cf. E. Jordis, *op. cit.*, p. 62, and the authorities there cited.	Usually smooth and soft: easy to finish. Uniform colour. Less likely to be pitted or to strip (or peel). Thick deposits easy to obtain.

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[1] The solubility of $NiSO_4(NH_4)_2SO_4\,6H_2O$ at 16° C. is 5·8 parts per 100 parts water; that of $NiSO_4\,7H_2O$ is 37·4 parts per 100 parts water. Roscoe and Schorlemmer, *Treatise on Chemistry*, 1907, vol. ii. p. 1282.

[2] The whole of the metal salt can be thrown out of solution by the addition of sufficient ammonium sulphate, *vide* Roscoe and Schorlemmer, *op. cit.*, p. 1282.

[3] For interesting information on anode efficiencies, *vide* O. W. Brown, *Trans. Am. Electrochem. Soc.*, 1903, vol. iv. p. 83.

[4] See Chapter II., p. 13.

NICKEL-PLATING SOLUTIONS

The recipes that have been proposed from which to prepare nickel-plating solutions are very numerous.[1] It may be said, however, that there are very few objects of nickel deposition that cannot be successfully achieved with the bath that is to be described in detail immediately, or some slight variant of it. It is, like the acid copper bath, one that is employable generally. For a few special purposes, for example, deposition on zinc[2] and, perhaps, aluminium also, a special and different type of bath may be more usefully employed. And again, for very heavy deposits (of the order $\frac{1}{8}$ in. to $\frac{1}{2}$ in., say), the solution may be preferably constituted as given in Solution 2.

Solution 1

(a) *Composition*

The constitution is as follows: 3 lb. of nickel sulphate; $\frac{1}{2}$ oz. of common salt; 1 oz. of boracic acid (powdered); and 1 gallon of water. This bath, or a variant of it, can be used for all "still vat" work, for barrel-plating, and for basket work. If the goods to be plated are heavy castings (or the like) with very irregular surfaces, the composition, as given, should be varied by the addition of more common salt, in order to increase the conductance of the solution. Thus, another $\frac{1}{2}$ oz. of salt per gallon may be added in such cases. Similarly, for barrel-plating, that is, the deposition of nickel (or other metal) on a quantity of small articles, such as screws, nuts, springs or buckles, enclosed in, for example, a circular or drum-shaped celluloid or wooden container (with holes pierced through the celluloid or wood), that can be rotated in the solution on a horizontal axis, the electrolyte may well be made more conducting by the addition of more salt, and be made to yield a still softer and whiter deposit by the addition of another ounce of boracic acid per gallon of solution. The variation of composition to be made in any special case (where it is necessary) is a matter to be left to the experience and discretion of the operator.

It will be interesting and instructive to consider briefly how far a solution of the composition stated conforms to the requirements of a good plating solution as described in Chapter IV. In the first place, it is to be noted that the composition is *simple*. There are only *three* substances present, namely (1) *the metal-containing salt* (nickel sulphate), (2) a *conducting salt* (common salt), and (3) the *boracic acid*. The electrode reactions that have to be considered are few in number, since the ions discharged are, almost entirely, the nickel ions, and the sulphate ions (or sulphanions, as they are sometimes called).[3] Essentially, one has to do with the electrolysis of nickel sulphate simply. The bath will, therefore, be easy to control. Next, the anode and cathode efficiencies approximate closely to 100 per cent.; hence the upkeep of the bath is practically automatic, if good anodes are used. It is rarely necessary to add metal salts: solution of the anodes supplies metal. Thirdly, the deposit is of close, fine-grained texture and, to the eye, non-crystalline: it is comparatively dense and non-porous. It becomes dull, soft, and smooth after deposition has continued for a short time; and, consequently, it is easy to finish. Lastly, control is rendered still easier and more intelligent by the fact that the function of each of the constituents is known. The functions of the nickel sulphate and sodium chloride are evident; that of the boracic acid is less so, perhaps. E. Weston,[1] who introduced the use of boracic acid in nickel baths, claimed that this substance (1) prevented the formation of sub-salts (including oxides) at the cathode, (2) reduced the evolution of hydrogen, (3) improved the physical character of the deposits, making them softer and whiter, and (4) improved the adhesion of the deposit to the base metal. Schlötter confirms most of these claims:[2] the author is also in a position to do so. He believes that the improvements indicated are simply due to the fact that the boracic acid, being very slightly ionized in solution, affords just sufficient hydrogen ions at the cathode to prevent the formation of oxides and hydroxides there, and the consequent deterioration of the deposit, but that the hydrogen ions are not sufficiently numerous to allow, after their discharge, of the inclusion of much hydrogen gas in the deposit, or materially to affect the cathode efficiency.

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[1] *Vide* E. Jordis, *op. cit.*, pp. 58 and 59, or W. G. M'Millan, *Electro-metallurgy*, 1910, p. 218.

[2] Vide *Metal Industry* (Amer. edit.), 1920, vol. xviii. p. 308.

[3] *E.g.*, by J. Walker, *Introduction of Physical Chemistry*, 1907, p. 225.

It may be remarked that no claim to originality is made in respect of the composition given above. All the substances have been used many times before in nickel solutions: they have been used both individually and in combination. There is nothing new in their use; but the good features of a solution composed of them do not appear to be generally known, and included among these features are the general utility, the efficiency, and the economical working of the solution.

(b) *Working Conditions*

These are: *Specific gravity*, 18° Bé. (about); *Current density*, up to 8 amp./ft.^{2}; E.M.F., *e.g.*, 2 volts, at 9 in. electrode distance, when 75 ampères were being used on fifteen handle-bars, 3 volts to give 120 ampères on 112 cycle cranks, the electrode distance being approximately the same; *Reaction*, very slightly acid.[3] Litmus (blue) should be turned to a dull, wine-red colour only—Congo paper must not be turned blue or even darkened; *Temperature*, above 60° Fahr.; *Anodes* of good cast metal should be used, and as many of them as the rods will hold; *Agitation* is, as always, an advantage, but it is not essential.

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[1] Amer. Pat. No. 211,071 (1878).

[2] *Galvanostegie*, Teil 1, 1910, p. 58, and vide *Brass World*, 1911, vol. vii. pp. 212, 234, and 317; but see *per contra*, E. Jordis, *op. cit.*, p. 60, and cf. also G. Langbein, *Electro-Deposition of Metals, sub. nom.* "Nickel." The recently-expressed views of M. Schlötter will be found in *Stahl u. Eisen*, 1921, vol. xli. at p. 273.

[3] This may be maintained by very small and careful additions of 10 per cent. (by vol.) sulphuric acid (pure), or better, by using larger amounts of boric acid.

It will be seen that the working limits of the solution are wide; and this latitude is, of course, a great advantage in works practice, and is yet another reason for preferring the single sulphate solution to that made up from the double salts, which, as O. W. Brown has stated,[1] has but narrow working limits.

(c) *Operation of the Bath*

There are no special rules required to work this bath: the general rules of practice set out in Chapter IV. suffice.[2] It may, perhaps, be well to remark that, sometimes, new solutions do not give of their best at the start. This feature is common to other solutions, and was noticed as long ago as 1858 in connection with solutions for depositing antimony.[3] It is not definitely established why this is so; it may be due to different causes, possibly, in different cases. The author believes it is often due, in the case of the single sulphate bath here considered, to the salts having been crystallized from an acid solution and insufficiently washed. He has, however, invariably found that where this feature occurred, the irregularity quickly disappeared as the result of a few hours' work with heavy current on scrap cathodes.

SOLUTION 2

(a) *Composition*

This bath is based upon the use of magnesium sulphate. A process for nickel deposition, where a solution containing this salt was used, has been patented by M. Kugel,[4] but this fact need not prevent one using similar solutions, for, even if the subject-matter of the patent was good in law, it is over twenty years old. A solution made up from the following constituents has given excellent results in practice: 3 lb. of nickel sulphate; 8 oz. of magnesium sulphate; and 3 oz. of boracic acid, dissolved in 1 gallon of water.[5] It will be noted that the amount of boracic acid is considerable, but that will not be found to be injurious.[6]

(b) *Working Conditions and* (c) *Operation of the Bath*

What has been said above in relation to Solution 1 applies here also—in general. A current density of 10 to 15 amp./ft.^{2} may be used, however even for long-continued deposition. The deposit has a somewhat bluish colour, which causes a plated article to look, to a critical eye, dark after buffing; whereas the deposit from Solution 1 is as nearly white as a nickel deposit can be.

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[1] *Op. cit.*

[2] These rules should be referred to again here.

[3] G. Gore, *Phil. Trans. Roy. Soc.*, 1858, p. 185 et seq.

[4] D.R.P. 117,054 (1899).

[5] The bath recommended by Kugel consisted of: 100 grms. nickel sulphate, 100 grms. magnesium sulphate, and 1 litre of water, for work at 90° C.

[6] Cf. *Brass World*, 1911, vol. vii. *loc. cit.*, and also C. P. Madsen, *op. cit.*

ANODES

In a former place it was stated that further consideration would have to be given to the subject of anodes: the present is a convenient place to do so. In ordinary works practice comparatively little attention is paid to the anode side of the plating tank, notwithstanding the fact that the proper functioning of the anodes is of the highest importance. The two chief functions of anodes are: (1) to lead the current into the solution, and (2) to feed the solution with metal. The ease with which the current can enter into a solution and the facility with which the anodes dissolve depend, so far as these are concerned, upon their shape, composition, and physical (metallographical) constitution. These three matters ought, then, to be regarded both by manufacturers and users of anodes; but it is doubtful whether much serious attention has been paid to them in this country.

(a) The Shape of Anodes

This has been matter for much controversy. Flat sheets (of various dimensions), corrugated sheets, and solid elliptical forms have, among others, been strongly advocated. As the result of a scientific investigation, C. F. Burgess and C. Hambuechen[1] came to the conclusion that, of the three types, the elliptical (or oval) dissolved most easily, and the flat anodes least readily, under the action of the current. They also showed that the oval anodes dissolve more evenly, and that, with that type, there was less waste or scrap than with the others. At the same time, it must be remarked that these workers do not enlighten one as to how wear, of the kind to which oval anodes are subject, affects the conductance of the anodes themselves and of the bath as a whole. Nickel anodes and the double sulphate of nickel solution were used by Burgess and Hambuechen for the purposes of their investigation; but the results are applicable generally to other metals and other solutions.

(b) Chemical Composition

Composition affects the readiness of solution of an anode to a very considerable extent, and, of course, its conductivity as well. If anodes of pure nickel were used, they would almost certainly become "passive" after being in use for a short time, and then would not dissolve at all: the same remark applies to anodes of some other metals, *e.g.* iron. In the cases of such metals it becomes, therefore, of importance to consider what other metals than the nickel, iron, and so on, should be contained in the anode in order to promote its solution, and what amount of this should be present in order to secure 100 per cent. efficiency. Obviously, the other metals must not be such as, on solution, would injure the electrolyte, nor should the less freely soluble (less electro-positive, that is) material be so easily detached from the anode sludge that it will form floating matter in the solution and become a cause of rough deposits. The whole matter is one inviting and calling for research.[1] Meantime, it can be stated that a nickel anode conforming to the composition given immediately has been found, in practice, to dissolve regularly and well, though the efficiency fell considerably short of the desired 100 per cent. The composition was: Ni, 97·23 per cent.; Fe, 0·88 per cent.; and the difference consisted of silica, carbon, and other insoluble matter.[2]

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[1] *Electrochem. Industry,* 1903, vol. i. p. 347.

(c) *Physical Constitution*

The physical constitution of an anode depends upon its metallurgical treatment, mechanical and thermal. It is commonly agreed that cast metal dissolves more readily than rolled, and that, in the case of nickel, electro-deposited metal is the least satisfactory from the point of view of its solution. These facts have been established for nickel and the double sulphate solution by W. Pfanhauser, jun.[3], and by [illegible] W. Brown.[4] But, assuming that a cast nickel anode is the most soluble type, research is still required in regard to the proper casting temperature, rate of cooling, and like matters. These factors will affect the size of grain of the cast anode, and in other ways influence its physical constitution; and it is well known that the solubility of substances in general and of metal in particular, depends upon size of grain and the like. It is quite possible—indeed, probable—that research in the direction indicated here, too, would lead to improvement in the solution efficiency of nickel anodes, even in the nickel ammonium sulphate solution.

NICKEL-PLATING DEFECTS

The last subject to be referred to is the defects to which nickel deposits are liable. The principal of them, their causes and their remedies or means of prevention, will be found in Table III.

REMARKS ON TABLE III

(1) A defect (or "trouble") may be due to two or more causes acting together, as, for instance, acidity and low metal content, which would give rise to excessive pitting. To find what the cause (or causes) is, the operator should work on 2 gallons of the solution only, as described in Chapter IV.:[5] causes (and remedies) should never be sought (or applied) by experimenting on the bulk. Moreover, proceeding in the way indicated saves time and material, and, further, encourages confidence. The practice of sending for an outside "expert," whenever

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[1] Cf. W. M'A. Johnson, *Electrochem. Industry*, 1903, vol. i. p. 48; *Trans. Am. Electrochem. Soc.*, 1902, vol. ii. at p. 173.

[2] On this subject, see the important results contained in C. P. Madsen's paper, already cited.

[3] *Zeit. f. Elektrochem.*, 1901, vol. vii. p. 698.

[4] *Op. cit.*

[5] *Sub nom.* "The Upkeep of the Solution."

TABLE III

DEFECTS OF NICKEL-PLATING

Defect.	Cause.	Remedy.
SPLITTING OR CRACKING	*Inclusion of hydrogen* (and, perhaps, of iron). Splitting may be due, and probably is due, at least in part, to the internal pressures or strains within the metal during deposition.—G. G. Stoney, *Proc. Roy. Soc.*, 1909, vol. lxxxii. p. 172.	Prevention, so far as possible, of evolution of hydrogen at the cathode by : (i) Employing a lower current density ; (ii) Increasing the conductivity, thereby decreasing the E.M.F. across the rods and probably also the cathode solution potential ; (iii) Increasing the metal content of the bath by (*a*) adding metal salts, (*b*) frequently cleaning the anodes, in order to facilitate their solution ; (iv) Employing a solution of such composition that no constituents which easily give rise to hydrogen formation are contained in it ; (v) Working at a sufficiently high temperature, *i.e.* above 65 Fahr. at the lowest.
PEELING OR STRIPPING	BAD CLEANING ; or *Too great acid content*, where the bath is "worked" on the acid side, or *Too high current density* ; or *Too cold a solution.* Again, peeling can be caused by *impurities* in the solution, *e.g.* (according to Schlötter), petroleum and other substances used in the preparation of the work.[1]	For all these causes of peeling the remedies are obvious. The only real remedy is to proceed thus : Fill up the cathode rods with scrap articles, and pass through the solution as much current as possible. Test, every now and again, for improvement in the deposit by suspending and plating a well-cleaned article in the solution. This remedy is sometimes called "Working out."
BRITTLENESS . .	(*a*) According to Schlötter (*op. cit.*), iron, petroleum, and organic substances (*e.g.* decomposition products of citric acid, etc.). (*b*) *Hydrogen.*	(*a*) "Working out" is the only remedy, and it is here an expensive one. (*b*) See under SPLITTING.

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[1] M. Schlötter, *Stahl u. Eisen*, 1921, vol. xli. p. 293.

TABLE III—*continued.*

Defect.	Cause.	Remedy.
Bad Colour— (i) Dark, black streaks, green or yellow (ii) Black streaks (iii) Bluish (iv) Grey-black	*Composition of bath or impurities. Too high current density.* (i) Alkalinity. (ii) Presence of copper or zinc. (iii) Magnesium salts. (iv) Too high current density.	The remedies in cases (i), (iii), and (iv) are obvious. (ii) Work out (*vide* Peeling). *N.B.—To detect copper.* Take 20 c.c. of solution, make the volume up to about 90 c.c. with water, and then add 5 c.c. H_2SO_4 (conc.) and 2 c.c. of HNO_3. Now pass a heavy current through the solution, using platinum electrodes—a clean Pt wire as cathode. Copper, if present, will be deposited as such; nickel cannot be deposited from the strongly acid electrolyte. *To detect zinc.* Take 20 c.c. of the solution, add strong ammonia till the precipitated hydroxide is redissolved, and then add citric acid solution till the solution reacts acid. Now pass H_2S gas. A white precipitate indicates zinc.—*Vide* Schlötter, *op. cit.*
Pitting	*Hydrogen* (i) Excessive. (ii) Slight.	(i) *Vide* Peeling. (ii) Agitate the solution; use moving roads; or tap the cathode rods sharply at intervals.
Lack of deposit in hollows	(*a*) *Poor conductivity,* due to (i) Original composition of the bath; (ii) Alkalinity. (*b*) *Low metal content,* due to poor anode efficiency. (*c*) *Acidity*—usually too great H_2SO_4 content.	The remedy is obvious in each case.
Roughness or Lumps	(i) *Particles,* floating about in the solution, settle on the articles being plated, and become incorporated in the deposits. (ii) *A too high current density* will cause a kind of roughness, but this kind differs from (i). It appears first on the ends of articles or on the parts of them nearest the anodes, whereas roughness caused as in (i) is felt on the upper surfaces of the goods, especially.	(i) (*a*) Keep the anodes clean. *Avoid dust.* (*b*) Do not disturb the vat sludge during work. (*c*) Keep the solution covered when the bath is not at work. (ii) Lower current density.

something goes wrong in the plating shop, is a thoroughly bad one. More often than not, the "expert" knows no more about plating than the man in the shop—sometimes, indeed, not as much.

(2) The defect that has been called "pitting" is sometimes referred to as "porosity." Pitting may, at times, be so bad that it makes the deposit porous, but in general it is not sufficient for that. Porosity, proper, is a characteristic of all (or almost all) electro-deposits, and is the result of their crystalline structure. As a rule, the more coarsely crystalline a deposit is, the more porous it will be.

(3) In connection with some of the defects mentioned in Table III., *e.g.*, irregularity of deposit due to poor conductivity or low metal content, some remarks of Schlötter (*op. cit.*) on nickel anodes are important. They are worth quoting *in extenso*, especially as they emphasize the importance of the anode question: they are certainly fully confirmed by the author's long practical experience. "Care must be taken," says Schlötter, "that as much nickel is dissolved at the anodes as is precipitated at the cathodes. Since, now, where rolled anodes are used, solution at the anode does not keep pace with deposition at the cathodes, cast as well as rolled anodes are employed. In this way the metal concentration is maintained at the desired strength. If rolled anodes only are used, the electrolyte soon becomes acid; while the sole use of cast anodes results in an alkaline bath. Since evolution of oxygen occurs at rolled anodes, nickel oxides are formed, and an oxidation of the whole anode surface takes place: they become decayed (*mürbe*) and spongy. This action is especially noticeable in cases of neutral or alkaline solutions: in acid solutions it is less so. The explanation is that with rolled anodes solution of them does not take place readily; on the contrary, so high a potential exists at the anodes that oxygen is evolved, and this causes oxidation of the metal."

REFERENCES

M. R. Thompson.—"The Acidity of Nickel-depositing Solutions," *Trans. Am. Electrochem. Soc.*, 1922, vol. xli. p. 333.

M. R. Thompson and C. T. Thomas.—"The Effect of Impurities in Nickel Salts used for Electro-deposition," *Trans. Am. Electrochem. Soc.*, 1922, vol. xlii. p. 79.

V. Kohlschütter and H. Schödl.—"Über die Struktur des elektrolytisch abgeschiedenen Nickels," *Helv. Chim. Acta*, 1922, vol. v. p. 490.

The following paper describes an interesting apparatus for research:

E. A. Vuilleumier.—"The Application of the Contractometer to the Study of Nickel-deposition," *Trans. Am. Electrochem. Soc.*, 1922, vol. xlii. p. 99.

M. R. Thompson.—"The Effect of Iron on the Electro-deposition of Nickel," A paper read before the *Am. Electrochem. Soc.*, May 1923.

CHAPTER VII

ZINC

THE literature relating to the electro-deposition of zinc is very considerable; and in it both electro-refining and electro-plating have received much attention. The former operation is not considered here:[1] attention is directed to the process known as "electro-galvanizing," the process, that is to say, which is concerned with the electro-deposition of zinc upon articles of iron and steel for the purpose of protecting them from the action of corrosive agencies, such as moist air and sea-water. The latter forms the sole use for electro-plating with zinc. Of all the metals that have been used to hinder the corrosion of iron and steel, zinc is certainly the most important and most effective. This fact would probably not be disputed by most of those with experience to judge; but there is some difference of opinion as to the best way of applying the zinc to the iron or steel. Three methods have been adopted in practice, namely: *Hot galvanizing*—that in which the article to be coated is dipped in or drawn through molten zinc; *Vaporization processes* (including Sherardizing)—wherein the articles to be coated are heated in contact with a zinc-containing compound or substance, such as the oxide or carbonate or other compound, and the vaporized zinc becomes deposited on the iron or steel;[2] and, lastly, *Electro-galvanizing*. It would be out of place to discuss in detail here the relative merits of these three processes. In general, it may with truth be said that no one of them is universally the best; whether this one or that should be adopted depends upon all the circumstances attending each particular case. Factors which, among others, have to be considered are: (1) The kind of metal to be treated—whether cast or rolled or drawn, case-hardened, tempered, and so on;[3] (2) the use to which the article is to be put, and here, especially, attention should be paid to any possible physical effects that the respective processes may have on the metallurgical condition of the articles; (3) the effectiveness—especially having regard to the particular case—of the processes respectively; and, particularly, (4) costs. While detailed discussion is avoided, it is of interest and value to refer to the opinions of such *impartial* authorities as Professor C. F. Burgess and Dr. W. Guertler. Burgess, as the result of a careful experimental investigation of the properties of zinc coatings, came to the conclusion that the principal fact brought out by his work was that "with the corroding agents adopted, electro-zinc has resistant properties far superior to zinc applied in the molten condition."[1] Dr. Guertler studied the micro-structure of galvanized iron, and found that the electro-deposited metal could, like the zinc applied by the other methods, be porous, and concludes that "an absolute superiority cannot be ascribed to any one of the three processes named."[2] It may be added that Dr. L. Aitchison has quite recently expressed the view that, in general, the electro-galvanizing process is to be preferred.[3]

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[1] The zinc extraction process (by electrolytic means) is also, at the present day, receiving more attention. For a recent and very full account of this, see S. Field, *Trans. Far. Soc.*, 1922, vol. xvii. p. 400.

[2] A multitude of patents relating to such processes have been granted. For example, in 1911 alone there are four, namely, Nos. 5811, 14,537, 16,294, 23,265.

[3] *Vide* L. Aitchison, "Electro-plating for the Prevention of Corrosion," *Trans. Far.* 1921, vol. xvi. p. 473.

PROPERTIES

The properties possessed by electro-deposited zinc depend upon the conditions under which it is formed, just as is the case with electro-deposits of other metals. But zinc appears to be especially sensitive to those conditions, among which the composition of the electrolyte is of great importance. The presence of any considerable quantity of mineral acid (sulphuric or hydrochloric) affects the properties of the deposited metal very markedly. Electro-deposited zinc can have almost any shade of grey colour. It can be bright or dull and matt. In macroscopic aspect it can be smooth and (apparently) non-crystalline, or it can be rough and quite coarsely crystalline, the individual grains being easily visible through a hand-lens. Under the microscope a polished and etched section always appears granular (crystalline), even in those cases where, to the unaided eye, the metal is bright and, seemingly, without crystalline structure. Sometimes, the deposit is powdery or spongy. In such cases it is probable that the deposit is not pure zinc, but consists of metal mixed with oxide or hydroxide, in the case of the powdery deposit, and of hydride of zinc (with, most likely, metallic zinc) in the case of zinc sponge.[4] The deposited metal is never really hard, in the same sense as is deposited iron, nickel, or cobalt; but it can be, and often is, very brittle, and this is especially apt to be the case where the deposit attains any considerable thickness. On the other hand, the metal can be so ductile that electro-galvanized copper wire can be wound round a 10-gauge wire without showing any sign of fracture.[5] Where the metal is bright, it tarnishes (oxidizes) in the air; and it is, of course, subject to the attack of acids, just as is ordinary zinc, though, being (usually) purer, the attack is less rapid.

ZINC-PLATING SOLUTIONS

A multitude of solutions have been proposed as suitable for electro-galvanizing. Among the best baths at present employed in works practice are to be numbered certain baths which are placed on the market under trade names, and the compositions of which are trade secrets. While it is a fact that a certain small number of these solutions have proved themselves of great use, yet it is also a fact that they suffer in practice from the defect common to all such baths, namely, that their compositions are unknown to those who have to work them. These are, therefore, handicapped in that they are more or less helpless when such baths "go wrong." Moreover, some of these baths are needlessly complicated in composition, and this, again, renders their operation more difficult. Almost all the solutions intended to be used for electro-galvanizing, that have been patented may be safely neglected by depositors. A few exceptions will, however, be mentioned. In 1908, E. C. Broadwell patented,[1] as assigner to J. W. Meaker, of Chicago, a solution containing zinc sulphate together with zinc naphthalene disulphonate. In the specification it is stated that "the proportions of the constituents may vary through a wide range dependent on the current and the purpose for which the deposit is required." This bath has been found to give excellent results on several classes of work; but it was also found that its conductance did not enable the re-entrant angles of such goods as iron window-frames (and the like) to receive really satisfactory deposits of zinc. Another solution worthy of mention here is that patented in 1905 by L. Trunkhahn and A. Neurath.[2] This bath is composed as follows: 25 kilo. zinc sulphate, 15 kilo. aluminium sulphate, 1 kilo. calcium carbonate, 4 kilo. maltose (or dextrine), ½ kilo. brewer's yeast, and 100 lit. water. The bath gives a good, smooth, *bright* deposit, when worked at 10 to 15 amp./ft.², gives good results over considerable periods of deposition, and, despite its complexity, does not seem to get out of order easily. It has been used for coating tubes, inside and out, the total costs of operation working out at 24s. per ton (pre-war). Both Dr. Peters, of Berlin, and Dr. I. Szirmay, of Buda-Pesth, have reported very favourably on the results they obtained from the bath. The two foregoing solutions suffer from the common defect that the composition is complex. What the reactions are which occur at anode and cathode, respectively, in a bath containing naphthalene disulphonates are unknown; and Dr. Peters and Dr. Szirmay have given different explanations of the manner in which the maltose and yeast affect the nature of the deposit. At the same time it is true to say that nearly all the really successful solutions used for electro-galvanizing[3] contain either a colloid, or sulphate of alumina, or other substance that produces the same effect on the deposit as many colloids do.[4] Many contain both. It is, unfortunately, just as true that, though much has been written upon the way in which colloids and quasi-colloids act in plating solutions, the only thing that is known for certain is that many of them appear to cause a cutting down of the size of the grains composing the deposits, and that this results in the formation of a smoother and denser (physically, more homogeneous) deposit. Why the grains are reduced in size—the cause or causes that operate to effect the reduction—is not known; nor is it known why one colloid will produce beneficial effects while another produces either no effect at all or, may be, a bad one. Professor Bancroft's view[1] that the "addition agent" (that is, the colloid) "involves the decrease in crystal size due to absorption of the addition agent" can scarcely be considered as more than a personal opinion. Under all the circumstances it is considered best, for present purposes, to divide zinc-plating solutions into two classes, namely, (1) Patented and (2) Non-patented solutions.

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[1] *Electrochem. and Met. Indus.*, 1905, vol. iii. p. 17.

[2] *Internat. Zeit. f. Metallog.*, 1911, vol. i. p. 353.

[3] *Loc. cit.*

[4] H. Danneel, *Handb. der Elektrochemie, Specielle Elektrochemie,* Teil 1, Lieferung 4, p. 301.

[5] Cf. I. Szirmay, *Zeit. f. Elektrochem.*, 1905, vol. xi. p. 333.

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[1] Amer. Pat. No. 905,837 (Dec. 8, 1908).

[2] D.R.P., No. 210,552 (1905); see *Jahrb. der Elektrochem.*, 1909, vol. xvi. p. 467.

[3] This statement is also true of many refining baths. For instance, The Anaconda Copper Mining Co., Great Falls, Montana, use glue (see *Amer. Inst. Min. and Met. Eng.*, 1921, vol. lxiv. p. 699, abstracted in *Mining and Metallurgy*, 1920, No. 168). Glue is, too, used at a zinc-refining works in Tasmania. On the other hand, D. McIntosh, who carried out some experiments at Trail, British Columbia, for The Consol. Mining & Smelting Co., states, as a conclusion, that "the solution should be absolutely clear and *free from colloids*" (*Trans. Roy. Soc. Canada*, 1917–1918, vol. xi. p. 118).

[4] Prof. W. D. Bancroft (*Trans. Am. Electrochem. Soc.*, 1912) appears to approve M. Schlötter's view that "the action of aluminium sulphate is clearly that of a colloid." See *Galvanostegie*, 1910, Teil 1, pp. 38 and 51.

1. *Patented solutions.* The two best of these have already been sufficiently commented upon. The only other one that seems to justify mention here is A. Classen's bath,[2] which has been investigated and commented on by S. A. Tucker and E. G. Thommsen.[3] Classen recommends the following bath: 100 grms. zinc sulphate, 20 grms. sodium sulphate, 5 grms. zinc chloride, 2½ grms. boracic acid, 25 grms. liquorice root (added gradually), and 500 c.c. water. Tucker and Thommsen found that the best current density to use is ½ amp./dcm.^{2} (about 5 amp./ft.^{2}) at ordinary temperatures; that it is necessary to add more liquorice root from time to time; and that agitation is beneficial. They state further that a bath composed of zinc sulphate and liquorice root gave equally as good results as that recommended by Classen.

2. *Non-patented solutions.* There is no intention to consider here even a few of the very great number of solutions that have been proposed for use in zinc-plating, and which have not been patented. The purpose here is to consider the making of a solution by those who do not wish to use one of the three patented ones described above. A certain type of solution is described, rather than an individual one. Though not of universal application, it is one that will serve many purposes, particularly if the quantities of its components be varied to suit different classes of work. At the outset the definite opinion is expressed that there does not exist a zinc-plating solution of the universal type—a solution, that is, that can be employed to best advantage in well-nigh all cases, in the same way as can the acid copper bath for the deposition of copper. The purpose the bath has to serve must, therefore, be carefully considered in each case: it rarely happens, for instance, that a zinc-plating solution suitable for tubes will do equally well for heavy castings.

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[1] *Chem. and Met. Eng.*, 1920, vol. xxiii. p. 454. A. Mutscheller's view is interesting, but hardly convincing (vide *Chem. and Met. Eng.*, 1915, vol. xiii. p. 353, and *Jour. Amer. Chem. Soc.*, 1920, vol. xlii. p. 2142). See also the following: E. F. Kern, *Trans. Am. Electrochem. Soc.*, 1909, vol. xv. p. 441; Wo. Ostwald, *Theoretical and Applied Colloid Chemistry*, 1917, p. 196; and O. C. Ralston, *Hydrometallurgy of Zinc*, 1921, p. 94 (McGraw, Hill & Co., New York).

[2] Amer. Pat. No. 809,492 (1906). A good review of zinc-plating solutions of all kinds, patented or otherwise, published before 1910, will be found in M. Schlötter, *op. cit.*, pp. 101 et seq.

[3] *Trans. Am. Electrochem. Soc.*, 1909, vol. xv. p. 477.

COMPOSITION

(*a*) *The metal salt.* Undoubtedly, zinc sulphate is the best metal-containing salt to use. It is cheap, and can be obtained commercially in a pure state;[1] it contains 22·78 per cent. zinc (metal); it is fairly soluble—3 lb. of salt (crystals), or even more, can be used for each gallon of water;[2] and the (SO_4)-anion attacks the zinc anodes well. Its solution is, however, a poor conductor; hence, a conducting salt must be employed.

(*b*) *The conducting salt.* Many substances have been used to aid the conductance of solutions based on the sulphate. Among these, the best are sodium sulphate (Glauber's salt), sodium chloride (common salt), magnesium sulphate (Epsom salts), aluminium sulphate, and zinc chloride; the last two have double purposes. The author prefers to use common salt.[3] This substance is cheap; its solution conducts well; and the chlorine anion helps to dissolve the anodes. The introduction of sodium complicates the reactions at the cathode, perhaps, but not more so than the magnesium or ammonium, where salts containing them are employed. Zinc chloride[4] is useful, but not easy to obtain cheaply in the pure state; moreover, it is not easy to use with accuracy. The author has always found it quite inadvisable to use sulphuric acid in electro-galvanizing baths; the principal reason is that the working of baths containing it is difficult to control on account of effects produced by it on the deposits when present in varying quantity, and it is always difficult to maintain the acid content constant.

(*c*) *Addition agent.* A bath composed of zinc sulphate and common salt only will not work well. One or more of the substances classed under the general term "addition agents" must be employed. For present purposes, boracic acid will be considered as such. Many authorities have used this substance,[5] and its addition is recommended here. W. Paweck,[6] who patented the use of boracic acid and other boron compounds in zinc baths, claims that it hinders the formation of zinc sponge. That may be so; but the author believes that it functions by preventing the formation of oxides and hydroxides at the cathode.[7] Another substance often added to zinc-plating baths, and recommended here, is aluminium sulphate.[8] This substance is also classed among conducting salts, and no doubt it does help the conductance of a solution; but, in view of its principal function, it must be classed among addition agents also. Its principal function is that it cuts down the size of the grains of the deposit (*vide* W. D. Bancroft, *supra*); this is a very important matter, as will be seen in connection with the structure of zinc deposits. The employment of this sulphate complicates, of course, the composition of the bath; but since its quantity in a solution remains approximately constant, the working of a bath containing it is not made more difficult from variations of content of the salt, and, in effect, the author has never met any difficulty occurring in a zinc-plating bath that could be traced to the use of aluminium sulphate. Of other substances used as addition agents in electro-galvanizing baths—substances such as gums, sugars, and the like—the following (in addition to those already mentioned) have been shown to give good results: Glue,[1] eikonogen,[2] pyrogallol,[2] beta-naphthol,[2] gum tragacanth,[3] gum arabic,[4] and the sugars (maltose, lævulose, dextrin, and others).[5] Of all these it has been found that the sugars give as good results as any. Their action is the same as that of aluminium sulphate; that is to say, they cut down the grain-size of the deposit, and often cause it to have a bright and even lustrous appearance. Used with the sulphate, they appear to act together with it in the direction indicated.

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[1] The purity of the salt used is of great importance. See S. Field, *op. cit.*

[2] 100 parts of water dissolve 50·88 parts $ZnSO_4$ at 15° C. Roscoe and Schorlemmer, *Treatise on Chemistry*, vol. ii., Metals, p. 650.

[3] This has been much used in zinc-plating baths.

[4] Langbein uses zinc chloride thus: 20 kilo. $ZnSO_4$ crystals, 4 kilo. Na_2SO_4, 1 kilo. $ZnCl_2$, ½ kilo. boric acid, 100 lit. water. Temp. ordinary for flat ware, 40° to 50° C. for other goods. C.D., about 20 amp./ft.^{2} And see E. F. Kern, D.R.P., No. 244,432 (1911).

[5] Cf. Langbein (note 4) and the Trunkhahn bath.

[6] Eng. Pat. No. 1688 (1902).

[7] Cf. Chapter VI. p. 62.

[8] Cf. (*inter alia*) the Trunkhahn bath. It is believed that the American Galvanizing Co. strongly recommend sulphate of alumina. See also: I. Szirmay, *Elect. Review*, 1903, vol. xliii. p. 850; *Zeit. f. Elektrochem.*, 1904, vol. x. p. 197; and I. Szirmay and L. von Kollerich, Eng. Pat. No. 16,959 (1900). For an explanation of the *modus operandi* of aluminium sulphate, see C. F. Burgess and C. Hambuechen, *Jahrb. der Elektrochem.*, 1902, vol. ix. p. 675; *Elektrochem. Zeit.*, vol. ix. p. 195; and *Electrical World*, 1902, vol. xl. pp. 411–416.

A solution made with zinc sulphate (at least 3 lb. per gallon of water), common salt (about 2 oz. per gallon), boracic acid (about 3 oz. per gallon), aluminium sulphate (3 to 4 oz. per gallon), and a sugar (maltose or dextrin), will be found to answer a great many purposes and be useful for galvanizing many classes of work. The quantities of common salt, aluminium sulphate, and sugar that may be used vary considerably;[6] but the quantities indicated will be found useful amounts to use. The quantity of sugar used is also variable: 1 to 3 oz. will usually be found sufficient. Such a solution does not answer the test of simplicity; but it is not so out of control as might, *prima facie*, appear. The function of each constituent is known, though how each does its work is not known in every case. The principal electrode reactions are liberation and solution of zinc; prevention of the formation of oxides (or hydroxides) by the boracic, and diminution of the size of the grains of the deposit by the aluminium sulphate are chemical and physical phenomena, respectively. As a matter of fact, though causes are either imperfectly understood or not understood at all, it has been found quite easy to work and control such a bath over long periods of time. This is, no doubt, the case largely because the anode and cathode efficiencies are high, being 96 to 99 per cent., working at 10 amp./ft.^{2}: the anode and cathode efficiencies are approximately equal; and, over periods of three hours' duration, and working at 10 amp./ft.^{2}, the bath gives uniform results.

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[1] *Mining and Metallurgy*, 1920, No. 168.

[2] O. P. Watts and A. C. Shape, *Trans. Am. Electrochem. Soc.*, 1914, vol. xxv. p. 291.

[3] Eng. Pat. No. 7255 (1911).

[4] J. Meurant, Eng. Pat. No. 21,149 (1900); D.R.P., No. 154,492 (1904).

[5] I. Szirmay and L. von Kollerich (*vide* note 8, p. 73).

[6] H. Paweck has noted the necessity of varying the amounts of the components of a zinc-plating bath to suit the work required of it. *Vide* Eng. Pat. No. 1688 (1902), or Amer. Pat. No. 745,378.

WORKING CONDITIONS

These have been indicated, namely, *Current density*, 10 amp./ft.^{2} (the E.M.F. at this C.D. will, of course, vary with the load, the material of the goods, rod distance, and other factors; it is usually from 2 to 2½ volts at a rod distance of 9 in.); *Temperature*, ordinary; *Agitation*, useful (as always), but not necessary. The *anodes* should be of good rolled zinc as pure as can be obtained commercially, and, in size and number, they should be as large and as many as the vat will accommodate.

OPERATION

The operation of zinc-plating baths in general is rather more difficult than is that of some others. In the case of a bath of the type described, there are two matters that require particular attention. It is of especial importance that goods should not be suspended in the bath unless current is passing or the goods themselves complete the circuit on and by their introduction into it. The solution has no cleansing properties—does not, that is, act chemically to remove oxide and other surface substance. The other matter relates to the formation of the deposit. It is observed, sometimes, that while the projecting parts of an article "strike" well, or, in other words, become quickly covered with a layer of zinc, the re-entrant portions and those farther removed from the anodes do not. These may even turn dark or black, and fail to "cover" even after deposition has proceeded for some time. This defect is, in most cases, due to one of three causes: Either the salts used to make the solution (*e.g.* the zinc sulphate or aluminium sulphate) contained *free* acid in consequence of not having been properly washed when crystallized during manufacture, or acid has got into the bath at some time subsequent to its making, or, thirdly, the conductance of the bath is too poor for articles of the kind that require, in the particular case, to be galvanized. In the two former cases, where the trouble is due to the presence of *free* (mineral) acid, the best remedy is that known as "working out";[1] in the last, more common salt must be added, using not more than ½ oz. per gallon of solution at a time.[2] In order to distinguish which of the possible causes is producing the defect, attention must be paid to the macroscopic aspect of the deposit. If the zinc, where deposited, is bright and metallic (while the bath is working at or below 10 amp./ft.^{2}), acid is causing the trouble.

Mastery can be obtained over the working of zinc-plating baths in only one way, which is outlined immediately. As already indicated, really good baths are, in the case of zinc, almost always of complex composition. Even if the function of each component is known, the minor electrode reactions are not. Hence, while he can be guided by his knowledge of the former, the operator must, in the present case, obtain his working knowledge of the bath from *working* experience. Working on the 2-gallon scale, he should make up a solution step by step, and find out by experiment and observation the deposit obtained at each step. For instance, he should dissolve the proper amount of zinc sulphate, and plate an article in the solution. Then he should add the common salt, plate another article (of the same kind), and compare results. The aluminium sulphate may then be added, another article (again of the same kind) plated, and, again, the resulting deposit compared with the former two. And so on. Another series of experiments can be made by altering the order of the addition of the components; and still a third by varying the amounts of each. In this way and by his observations on the electrode phenomena (evolution of gas, rate of striking, and the like) and current conditions, the operator will become self-reliant and, before long, a master of the working of his bath. For this purpose, *he must know what the components of the bath are*, and, so far as possible, *how each functions*. It is in this respect, especially, that a man working a solution of the type described is better off than if he has to work one of unknown composition. Such work as this can be quite well done during working hours in the shop. It ought to be done in the case of any plating bath, if the operator wishes to put himself in the independent position of being able to manage his own baths without outside help. It *must* be done in the case of a zinc-plating bath, if the operator is to be capable of meeting successfully any difficulties that arise.

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[1] Chapter VI. p. 66, Table III., *sub* "Remedy."

[2] *Mem.* Rules relating to additions, *sub nom.* "Upkeep of the Solution," p. 38 *ante.*

DEPOSIT

The deposit from a bath of the type under consideration has a greyish-white colour, tinged with blue. It usually possesses a brightness of a nacreous kind; but the deposit is still good if dull in colour and rather more blue. It has no apparent structure as seen with the naked eye: it does not look crystalline at all. It adheres quite well. The metal is as ductile as most samples of electro-deposited zinc, but if the current density is pushed too high, and the deposit becomes too thick, there is a tendency to brittleness. Agitation helps to prevent this; but thick deposits of zinc are not necessary for galvanizing purposes,[1] and the bath will be found fast enough (for ordinary work) at the working current density recommended.

STRUCTURE

It is quite true to say that, hitherto, very little attention has been paid by practitioners to the structure of zinc deposits in relation to their service as protectors of the underlying iron or steel. How various the structure may be is partly shown by the illustrations. The micrographs show, in particular, how great the effect of the composition of the bath

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[1] The *Bureau of Standards* (Washington), Circular No. 80, says that a thickness of 0·0015 in. is sufficient for most purposes. The author's experience is that considerably less (half to three-quarters of a thousandth of an inch) is sufficient for very many. The (average) thickness of a deposit of zinc is rather more than 0·001 in. per hour, working at 20 amp./ft.^2; hence the time required for 0·0015 in. is 1½ hours at this current density.

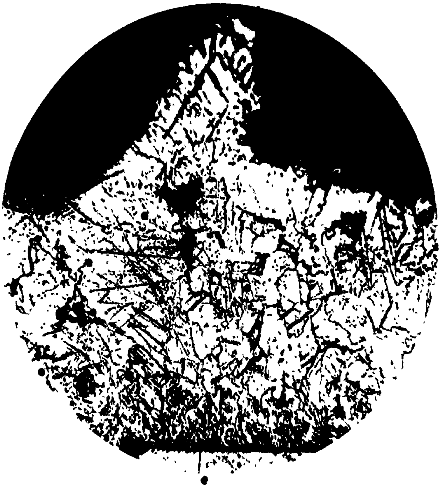

Fig. 18. × 150.

Solution: Zinc sulphate only.

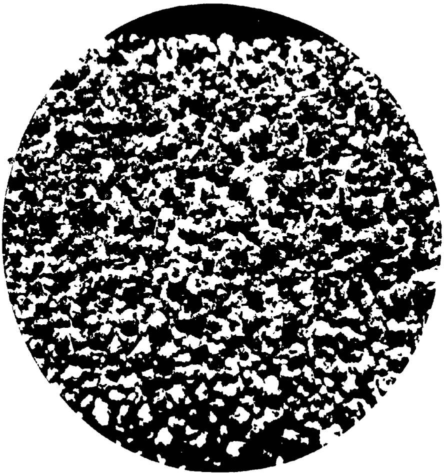

Fig. 19. × 15.

Surface of deposit of Fig. 18.
(Oblique illumination.)

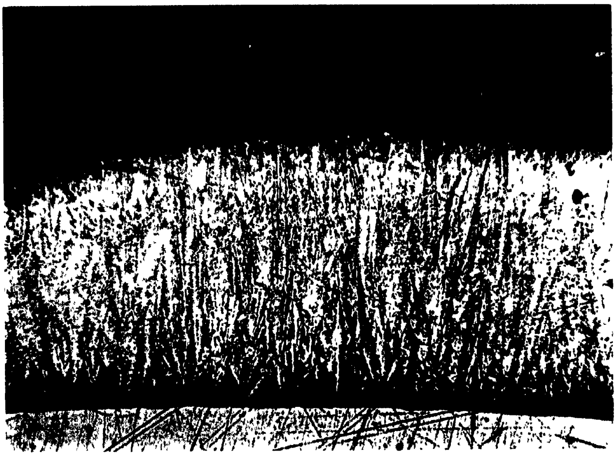

Fig. 20. × 150.

Solution: Zinc sulphate and free acid.

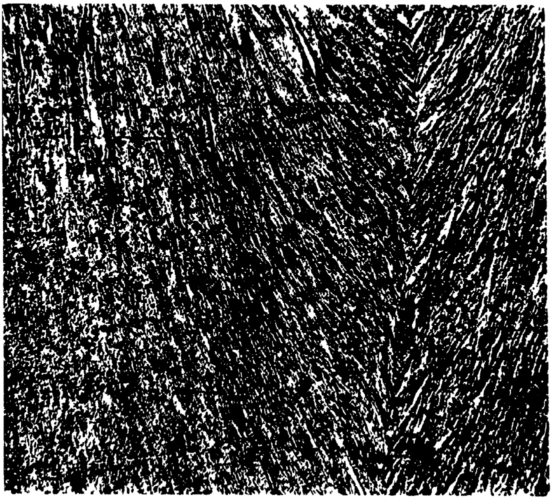

Fig. 21. × 160.

Solution: Zinc sulphate, free acid and gelatin

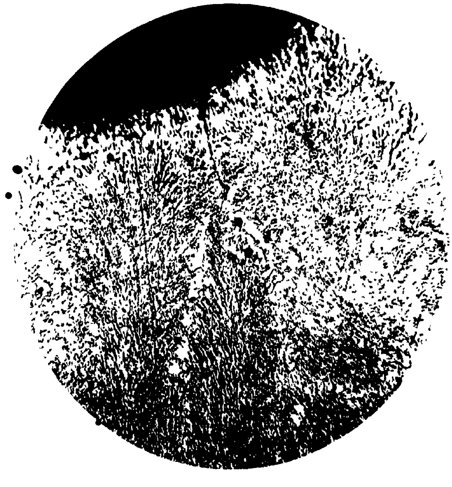

Fig. 22. × 150.

Solution: similar to Fig. 21.

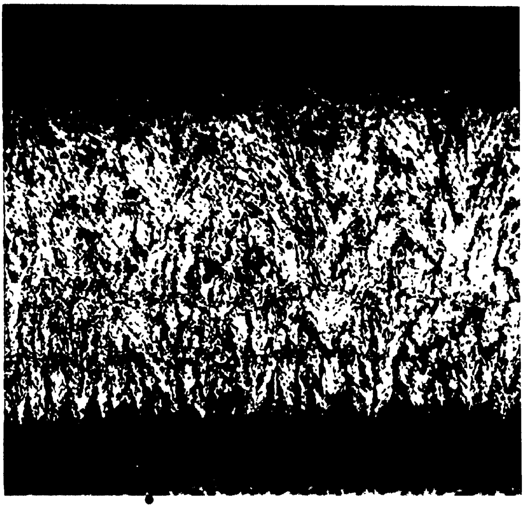

Fig. 23. × 150.
Solution: Zinc sulphate and dextrin.

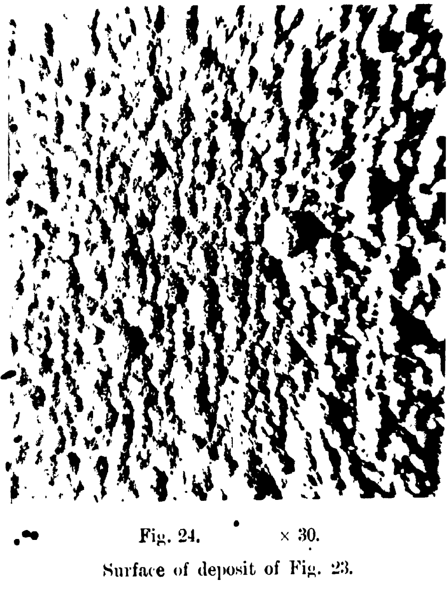

Fig. 24. × 30.
Surface of deposit of Fig. 23.

may be upon the structure of the deposit obtained. No account has been taken of varying conditions of deposition, which themselves occasion variations in the structures of deposits from one and the same bath. The deposits shown in the figures were (except that of Fig. 21) all formed under the same temperature, current density, and other conditions.

The Illustrations

Fig. 18.—This shows the structure of a zinc deposit formed in a bath containing the sulphate of zinc only. The surface of the deposit is holo-crystalline, and contains idiomorphic forms: the interior is hyp-idiomorphic. Such a structure renders the deposit useless for rust prevention. It is full of holes and oxide (black patches in the figure) and intergranular cracks.

Fig. 19.—In this figure the surface of the deposit, of which the interior structure is exhibited in Fig. 18, is shown.

Fig. 20.—The deposit was formed in a similar bath to that used for the deposit shown in Figs. 18 and 19, except that free sulphuric acid was present. The deposition conditions were alike in all respects in the two cases. It is notable that the acid has brought about a marked reduction in the form and size of the grains of which the deposit is composed. So far as structure is concerned, such a deposit is much less porous than that of Fig. 18.

Fig. 21.—This micrograph shows the type of structure a sound and useful deposit should possess. It was formed in a bath containing zinc sulphate, a slight amount of *free* acid (sulphuric) and glue.

Fig. 22.—The deposit here shown was, too, formed in a bath of similar composition to that used for the deposit of Fig. 21. But, while the former was made in this country, the latter was deposited in Tasmania.

Fig. 23.—The bath in which the deposit here shown was formed contained zinc sulphate and dextrin. The conditions of formation were the same as were used for the deposits of Figs. 18 and 20. The change of structure brought about by the dextrine is very marked.

Fig. 24.—This micrograph shows the surface of the deposit of Fig. 23; it should be compared with Fig. 19.

General Remarks

In general, the micrographs speak for themselves; the different structures obtained in consequence of the presence of different substances in the bath are most marked. Two points may, however, be specially noted: (1) Macroscopic features correspond (as is, indeed, to be expected) to micro-structures. (Compare Figs. 18 and 19 with 23 and 24, respectively.) This fact helps one to know what the latter is from visual observation of the deposit during its formation. (2) The structure a deposit possesses is not a matter of chance, but depends upon all the conditions of its formation and, especially, upon the composition of the solution in which it is formed. The deposit shown in Fig. 21 was made at the other end of the world in a bath containing sulphate of zinc, sulphuric acid, and gelatin. That of Fig. 22 was recently formed in this country in a bath of like composition. The finely fibrous structure which the deposits have in common is characteristic of *all* deposits formed in baths containing, as components, the three substances mentioned. It may be added that Dr. McIntosh has published a series of beautiful photographs that show the surface features of zinc electro-deposits under various conditions of deposition.[1]

MECHANICAL AND CHEMICAL TESTS

The testing of zinc deposits is a large subject, and cannot be fully treated here. The tests enumerated will be those that can be fairly described as satisfactory workshop ones—tests that can be carried out by any one in the workshop, and which, at the same time, give a sufficiently good idea as to the serviceableness of a deposit. They may be divided into two groups, namely: (1) Mechanical, and (2) Chemical; and they aim at determining (in an approximate way) the following "properties" of zinc deposits, namely, adherence, ductility, or brittleness, durability, uniformity, and porosity.[2] Table IV. contains a fairly complete classification.

Mechanical Tests

The following four tests were recommended [3] to and adopted by the Electro-Metallurgical Committee, Ministry of Munitions, as suitable *workshop tests* for adherence in connection with iron deposition; and they were found to give a sufficient degree of satisfaction for workshop purposes. These tests are: (*a*) The Saw test; (*b*) the Hammer (or Impact) test; (*c*) the Squeezing test; and (*d*) the Grinding test. (*a*) In this test the plated article is placed in a vice, and sawn through with a hack-saw. (*b*) In this test, the plated article is struck glancing blows with a hammer having a 1-lb. head. (*c*) Here, the article, where suitable, *e.g.*, a tube, is held in a vice, and squeezed until the distance between the jaws of the vice is diminished by about 50 per cent. (*d*) In the grinding test, the deposit is ground through by a dry emery wheel of some 6 inches diameter and rotating at about 1500 R.P.M. W. A. Macfadyen, who employed these tests, at the author's instance, reported that, while the squeezing test was found to be very stringent, and the grinding test least so (most of his iron deposits standing the grinding test well), the impact or hammer test was found to be a good one.[4] It is suggested that the saw test helps one to obtain an approximate idea of the brittleness (or powderiness) and toughness of a deposit. Nothing more is claimed for these tests than that they afford a fair estimate, for practical purposes,

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[1] *Trans. Roy. Soc. Canada*, 1917–18, vol. xi. p. 113.

[2] Cf. M. Schlötter, *op. cit.*, p. 114, and L. Aitchison. Also see W. Blum, *Trans. Am. Electrochem. Soc.*, 1919, vol. xxxvi., at p. 215, and W. Blum, F. J. Liscomb, Z. Jencks, and W. E. Bailey, *ibid.* at p. 253.

[3] By the author.

[4] *Trans. Far. Soc.*, 1920, vol. xv. p. 100.

TABLE IV

TESTS FOR ELECTRO-ZINC DEPOSITS

A.—WORKSHOP METHODS.

1. *Mechanical.*

Test.	Property tested.
(*a*) Saw	Adherence, brittleness, fragility, ductility.
(*b*) Hammer (impact)	,, ,, ,, ,,
(*c*) Squeezing	,, ,,
(*d*) Grinding	,, toughness.
(*e*) Bending	,, ductility.

2. *Chemical.*

(*a*) Copper sulphate (saturated, neutral) (*Preece*)	(*a*) Gross variation of thickness of the deposit. (Very roughly) weight of zinc per unit area.
(*b*) H_2SO_4 (3·2%) (*Burgess*)	(*b*) Variation of thickness. (With some approximation) weight of zinc per unit area. (Approximately) total weight of deposit per unit weight of base metal—iron or steel.
(*c*) Caustic soda (*Walker*)	(*c*) Porosity.
(*d*) Salt spray	(*d*) General resistance to corrosion.

B.—LABORATORY METHODS.

1. *Physical.*

Property tested.	Method.	Reference.
Adhesion	The method consists in soldering to the zinc surface, by means of a low melting-point solder, a copper plug ½ inch in diameter. By noting on a spring balance the pull necessary to separate this plug from the iron, a measure of the adherence of the zinc to the iron is made.	C. F. Burgess, *Electrochem. and Met. Eng.*, 1905, vol. iii. p. 17.

2. *Chemical.*

General resistance to corrosion (*C. L. Campbell*)	The zinc coating is dissolved off by a standard solution of acid, and the hydrogen generated and evolved is collected in a suitable apparatus. The rate of formation of the gas is presumed to be inversely proportional to the resistance to corrosion.	*Electrochem. and Met. Eng.*, 1909, vol. vii. p. 441.

of the properties in general and, especially, of the adherence of a deposit, whether of zinc or other metal. They should be used in conjunction with other tests, among which may be mentioned the *bending* test. This, like the squeezing test, can be applied to such articles only as possess the requisite shape, *e.g.*, tubes, sheet, and the like. It consists in bending the article (holding it in a vice, if necessary) so that one part is bent over towards the other through a right angle at least, and examining the deposit on the surface of the bent portion for fractures. A form of the test was used for testing galvanized wire by I. Szirmay.[1]

CHEMICAL TESTS

These require somewhat fuller treatment, as it is necessary to show clearly what each really indicates.

(*a*) *The Copper Sulphate Test*

This has been, variously, called Preece's; the Admiralty, and the Post Office test. It consists in dipping the zinc-coated article in a saturated and neutral solution of copper sulphate for a certain period of time (half-second, one second), taken as the unit, holding it, after removal from the sulphate, under a water tap giving a flow at full pressure, and noting how many such dips can be given before a firmly adherent coat of copper becomes deposited upon *the iron or steel base.* The method (as used at the Bureau of Standards, Washington)[2] of preparing the copper sulphate solution is as follows: 36 parts of commercial copper sulphate crystals are dissolved in 100 parts of water, and then some cupric oxide added to neutralize any free acid. The solution is diluted with water till its specific gravity is 1·186 at 18° C. Precautions that must be taken when applying this test are: the zinc must be free from grease, oil, and the like; the solution must be quite neutral—free, that is, from mineral acid, *e.g.*, sulphuric; and a careful distinction must be made between the dark, loosely adherent copper that forms on zinc by exchange and which a fast-running stream of water will wash away, and the reddish, clean-looking (sometimes bright) deposit of copper that is formed, also by exchange, upon iron or steel. It is the latter that must be looked for. Messrs. Watt and Philip say:[3] "It is necessary to carry out tests by this means with caution, or misleading results will be obtained." The unit of time often employed is one minute. It is stated by the same authorities that the amount of zinc required to be present on the surface of an electro-galvanized article, so to protect the iron or steel that it will withstand one 1-minute dip or immersion in the saturated copper sulphate at 15° C., is about 0·166 oz. per square foot of surface, while that required when the hot process is used is 0·248 oz. The reason for this difference is said to be the greater purity of the electro-deposited zinc. This test has been critically examined by several investigators:[1] it has been found to mislead, even when carefully carried out, and it cannot help misleading, if more is expected of it than that it shows whether the zinc is of even thickness all over the surface of the plated article. Really it is not necessary to prove this, for one knows it *a priori*. All, then, the Preece test shows one is whether there are considerable variations of thickness, or whether this is the same, approximately, all over the surface of the plated article. It *is* satisfactory for that purpose, and that is all. A few reasons why the test cannot give more information are the following: (i) The loosely adherent layer of copper that commences to be formed upon the *zinc* as soon as immersion occurs protects, in varying measure, the remaining underlying zinc, and thus causes the velocity of the reaction to be very irregular, so that it is quite impossible to say what quantity of zinc is dissolved in a certain unit of time. It is therefore, with rough approximation only, true to say that one can estimate the weight of zinc per unit area from the number of dips given. (ii) The velocity of displacement of copper by zinc depends upon (*inter alia*) the concentration of the copper in the solution. This is continually diminishing as copper is displaced and zinc goes into solution. The rate of diminution will vary with such conditions as volume of solution employed, temperature, and others. Hence, irregularity occurs from these causes also. (iii) The copper forms with zinc a zinc-copper couple, which acts (again irregularly) to disturb the uniformity of the velocity of reaction. (iv) The actual carrying out of the test is not so simple as it would appear to be. The copper sulphate solution *must* be neutral; and some investigators find difficulty in distinguishing between the loose copper deposit formed on zinc and the adherent deposit formed on the iron or steel. Moreover, according to Schlötter,[2] an adherent copper deposit can be formed on the zinc itself, which, therefore, does not, in cases, become completely dissolved or, at any rate, dissolves, as to part of it, very slowly.

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[1] *Vide supra, sub nom.* "Properties."
[2] *Bureau of Standards,* Circular No. 80, p. 23.
[3] *Electro-Plating,* 1902, p. 633. (Crosby, Lockwood & Co.)

It may be added that the copper sulphate test has been dealt with at length here because it has been found that that is the one used, almost exclusively, in this country, and used without much understanding of its value. This is, as a rule, exaggerated; as a matter of scientific fact, it has very little value.[3]

(*b*) *The Sulphuric Acid Test*

It was in consequence of the unsatisfactory nature of the Preece test that C. F. Burgess[4] proposed the use of a dilute solution of sulphuric acid in place of copper sulphate.[5] Schlötter, Halla,[6] and many others have used this solution on account of the uncertain results given by copper sulphate. This test consists in immersing the galvanized article in a 3·2 per cent. (⅔ Normal) solution of pure sulphuric acid.[1] It can be used for more accurate work than can the Preece test; but it is suggested that its chief use in the workshop is that, by means of it, one can observe the uniformity of the thickness of the zinc deposit much more exactly than the Preece test allows. When acid of the strength given is used, a stream of hydrogen gas is evolved from the surface of a galvanized article immersed in it. But as soon as the zinc is dissolved from any part of the surface, the evolution of gas ceases there. Thus, one can easily tell where the deposit is thicker, and where it is thinner; and the cessation of the evolution of bubbles is so marked that small differences of thickness (amounting to no more than a fraction of a thousandth of an inch) can be readily detected. As regards more accurate work, the average weight of zinc per unit area, or the total weight per unit weight of iron, can be determined with considerable accuracy, as can be seen in Table V., which contains the results of actual determinations made in the author's laboratory.

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[1] For instance, I. Szirmay, *Zeit. f. Elektrochem.*, 1905, vol. xi. p. 333, and M. Schlötter, *op. cit.*, p. 115. See also Note 3 *infra*.

[2] *Op. cit.*, p. 115.

[3] The Preece test has been condemned, on account of its irregularities, by a Committee of the American Society for Testing Materials. See *Proc. Am. Soc. Test. Mat.*, 1911, vol. xi. p. 100, and *ibid.*, 1917, Part I., p. 144.

[4] *Electrochem. and Met. Indus.*, 1905, vol. iii. at p. 18.

[5] *Op. cit.*, p. 115.

[6] *Zeit. f. Elektrochem.*, 1913, vol. xix. p. 222.

TABLE V[2]

WEIGHT OF ZINC DEPOSITS ON SMALL ARTICLES

Article.	Weight before Stripping (Grammes).	Weight after Stripping (Grammes).	Deposit (Grammes).	Remarks.
Small buckle	17·4548	17·2312	0·2312	All these buckles were plated at the same time in a barrel containing a 40-lb. load.
" "	18·0721	17·8411	0·2310	
" "	17·9932	17·7627	0·2305	
" "	17·8102	17·5790	0·2312	
" "	17·6170	17·3780	0·2390	
" "	17·7300	17·4907	0·2393	
French nails	11·3268	11·2496	0·0772	Two samples from the same load.
" "	11·1016	11·0240	0·0766	

(c) *The Caustic Soda Test*

This was proposed by W. K. Walker,[3] and forms a very useful test of the porosity of a zinc coating. "If a piece of zinc be placed in a strong solution of caustic soda, heated to about 100° C., no action is noticeable. If, now, the zinc be touched with a piece of iron, hydrogen is liberated in great volume *from the iron.* That is, iron in contact with zinc in strong, hot, caustic soda is a seat for the formation of hydrogen. Hence, if a piece of galvanized iron free from pin-holes and cracks be so treated, no action is visible; if the iron be exposed, however, to even a minute degree, a fine stream of hydrogen bubbles will be seen arising from the surface. Small cracks in the zinc surface may easily be detected in the same way."[1] It can be stated by the author that this test is quite a good one for the purpose it is required to serve—the detection of porosity; and it can easily be carried out in any plating shop.

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[1] Such a solution contains 3·2 grms. per 100 c.c. solution. It can be made, with sufficient accuracy for its purpose, by measuring out 1·7 c.c. of acid (of spec. grav. 1·84) and making the volume up to 100 c.c. with water.

[2] Cf. F. Halla, *op. cit.*

[3] *Proc. Amer. Soc. Test. Mat.*, 1909, vol. ix. p. 430; *Electrochem. and Met. Eng.*, 1909, vol. vii. p. 440 (abstract).

(*d*) *The Salt Spray Test*

As carried out at the Bureau of Standards, Washington, the test ". . . is made in an Alberene[2] stone box, with a cover and glass supports for the samples. The stone box is inclined so that drops of solution collecting on the cover will run down to the edge instead of dripping on the samples. A 20 per cent. solution (by weight) of commercial sodium chloride (20 grms. salt and 80 c.c. water, or 2 lb. salt and 1 gal. water), filtered if necessary, is used and, with an air pressure of about 6 or 7 lb. per sq. in., a very fine mist is produced. The compressed air is passed through a glass-wool or cotton plug, and then through water to remove any dust and to saturate the air with water vapour which prevents concentration of the salt solution and crystallization of the salt on the tips of the atomizer. A baffle plate is used to prevent the salt spray from blowing directly against the test pieces. The samples, after being washed with gasolene and ether to remove all grease, are placed in the spray box in a vertical position on the glass rods or strips. They are removed from the bath every twenty-four hours, washed with water, using a moderately stiff bristle brush,[3] and after drying carefully examined for the presence of red or yellow iron rust. The first appearance of rust indicates the conclusion of the test, but valuable information may be obtained by continuing the test and observing the extent of the corrosion produced by longer exposure."[4] The Circular states further: "The salt spray test as a measure of the relative value of zinc coatings depends on the time required for the complete removal of the zinc at the thinnest points, which is usually indicated by the appearance of iron rust. . . . Although the salt spray test is subject to many objections, it may be regarded as the best test for zinc coatings that has yet been devised. It is especially useful in determining the relative value of zinc coatings for marine exposure. No definite statement can be made about the life of zinc coatings in this test, but in general a sample showing rust spots in less than one day (twenty-four hours) should be regarded as unsatisfactory, while a life of two or three days would indicate a coating that could safely be used under moderate conditions of exposure, and a life of at least four to six days should be required for severe conditions of exposure."

Of the four chemical tests enumerated, the fourth only (the salt spray test) can be said to submit the galvanized articles to conditions in any way resembling those to which such goods will be subjected during their life. The first three are certainly much more severe than anything to which the zinc will be exposed; number four gives an approximate idea as to how articles will behave when exposed to natural corrosion agencies such as, for instance, those by which ships and sea-planes will be attacked. The spray test is, therefore, to be preferred as the test relating to resistance to corrosion; the remaining three should not, strictly, be regarded as corrosion tests at all, but as tests indicating the uniformity of thickness, purity, and porosity, of a zinc coating, while numbers two and three are, as well, useful means of enabling the coating to be removed for the purpose of weight determinations.

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[1] *Proc. Amer. Soc. Test. Mat.*, 1909, vol. ix. p. 430; *Electrochem. and Met. Eng.*, 1909, vol. vii. p. 440 (abstract).

[2] If Alberene stone is not available, the box may be made of glass, stoneware, porcelain, water-proofed wood, or any other insoluble and non-corrodible material. All connections should be of glass or rubber.

[3] Brushing seems a very inadvisable proceeding—to the author.

[4] *Bureau of Standards*, Circular No. 80.

REFERENCES

The following papers, additional to those cited in the notes to this chapter, will be of interest to those engaged in research—some of them, indeed, will help the practical man:

M. Gogon and M. Lemarchands.—" L'éléctro-metallurgie du Zinc," *Chim. et Indus.*, 1922, vol. viii. p. 506.

This paper contains a bibliography of the subject, a critical comparison of methods of deposition, and other useful matter.

J. T. Ellsworth.—" The Effect of Single Impurities on the Electro-deposition of Zinc from Sulphate Solutions," *Trans. Am. Electrochem. Soc.*, 1922, vol. xlii. p. 63.

W. G. Traub.—" Electro-plated Zinc and the Diffusion of Electro-deposits into Zinc," *Trans. Am. Electrochem. Soc.*, 1922, vol. xlii. p. 55.

G. D. Scholl.—" Effect of Impurities on Electrolytic Zinc," *Chem. and Met. Eng.*, 1922, vol. xvi. p. 595.

This paper contains a beautiful series of photographs showing the surfaces of deposits of zinc from baths containing known impurities in known amount. It is a most important paper to the practitioner. C. A. Hansen's remarks on Scholl's conclusions (*Chem. and Met. Eng.*, 1922, vol. xxvii. p. 100) should be referred to.

W. Blum, F. J. Liscomb, and C. M. Carson.—" Zinc Cyanide Plating Solutions," *Bureau of Standards*, Technical Paper No. 195.

This is a paper that seems to advocate the use of cyanide solutions for the deposition of zinc. (See remarks on Wernlund's paper, *infra.*)

C. J. Wernlund.—" Studies on the Zinc Cyanide Plating Solution," *Trans. Am. Electrochem. Soc.*, 1921, vol. xl. p. 257.

In the discussion on this paper (at p. 282), the present author has expressed his views as to the use of cyanide baths for electro-galvanizing. These are in opposition to the advocacy of Wernlund. Nevertheless, the paper is (as A. G. Betts says, p. 284) a record of " careful and thorough work," and " should be of great value in the electro-plating of . . . zinc." The present author believes that a worker should have the advantage of all the views expressed on the subject of his studies, whether he himself agrees with some of them or not: he is unwilling to follow the practice adopted in certain quarters in America, namely, that of attempting to suppress the expression of opinions that are contrary to one's own.

W. G. Horsch and T. Fuya.—" A Study of the Throwing Power and Current Efficiency of Zinc Plating Solutions," *Trans. Am. Electrochem. Soc.*, 1922, vol. xli. p. 363.

U. C. Tainton.—" Hydrogen Over-voltage and Current Density in the Electrodeposition of Zinc," *Trans. Am. Electrochem. Soc.*, 1922, vol. xli. p. 389.

CHAPTER VIII

LEAD

IT seems appropriate to consider the electro-deposition of lead next in order after that of zinc, since the principal purpose of lead-plating—as distinct from lead-refining—is protective. A few years ago authors of text-books were wont to dismiss the subject (if they mentioned it at all) in a few words contained in a later chapter. The reason for this is twofold: in the first place, it is only during the last fifteen years or so that there has been much information available relating to the electro-deposition of lead, and, in the next, information, as and when it was gained, had had no time to get into text-books. which, as far as those dealing with electro-plating is concerned are, for the most part, of the "paste and scissors" type. No serious writer on the subject of electro-plating in general ought, at the present day, to neglect the metal lead. It is, almost entirely, to the credit of A. G. Betts and F. C. Mathers[1] that the electro-deposition of lead is, to-day, a comparatively simple operation to perform successfully. Moreover, the use of lead for protective purposes is by no means to be neglected. It is true that lead, like nickel and unlike zinc, is electro-negative to iron, and hence cannot protect iron (or steel) as zinc can. But the form in which lead can be deposited, nowadays makes it a good *covering* for the underlying iron; it can and does prevent the access of the agents of corrosion, and thus hinders corrosion in the same way as does a varnish and some paints. The advantages of lead, as compared with other metals, are: (1) It is cheap, as compared with copper or nickel. (2) It is malleable. This enables articles to be "worked," after the lead coating has been put on, without such risk of fracture and, consequently, exposure of the subjacent iron as exists in the cases of most other metals. (3) Lead is much more resistant to acid fumes and similar corrosives than copper and even nickel. It is for this reason that lead is employed in chemical works and laboratories. As compared with zinc, lead has one great disadvantage. While it is as cheap or even cheaper than zinc, and much more malleable, it has no inherent capacity to protect iron. If the lead coating contains cracks or holes, the subjacent iron or steel will rust, whereas a zinc coating will protect the underlying metal, even though it contain fine cracks or very small holes. W. Lange[2] has recently published some results he obtained when investigating the resistance of sheet iron coated with lead, tin, and aluminium respectively. He found that lead electro-deposited from *acid* solutions (phenol sulphonic or fluosilicic), showed good resistance to corrosion in both tap water and half per cent. salt solution; but he found that, while lead deposited from *acid* solutions protects the underlying iron better than that sprayed on by Schoop's process, yet the protection of the iron from rusting obtained for comparatively short periods of time—the comparison being with the period of protection afforded by zinc coatings.

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[1] *Vide post.*

[2] *Zeit. Metallkunde*, 1921, vol. xiii. p. 267.

APPLICATIONS

Already, some years before the late war, lead-plating had commenced to come into use, in this country, for coating nuts, screws, and other accumulator parts. These goods were often made of brass, and it was found quite easy to lead-plate such small articles in bulk—in baskets, for instance, properly wired for the purpose. This method saved the labour and expense of separately wiring the articles. The war has undoubtedly urged forward the claims of lead deposition; but it is too much to say that "lead-plating was one of those industries which were developed as a commercial possibility as the result of military need."[1] A number of applications of lead-plating were mentioned by A. G. Reeve and others[2] in a paper presented some little while ago to the American Electrochemical Society. It may be helpful and suggestive to draw attention to them here. Reeve describes the electro-deposition of lead upon the inside of 4·7 inch (and other calibre) shells. Catalyser boxes, having an inside surface of 50 sq. ft. or more, have been plated with as much as 275 lb. of lead, which represents a thickness equal to about seven-hundredths of an inch. Another application has been to lead-plate the interior of common shell *in order to bring an under-weight shell up to standard.* This is analogous to the "building up" work done with iron. G. B. Hogaboom[3] states that "in butt-welding of the booster base on to the adapter, there was some thought that there might be an oxide of iron formed, and that would be attacked by the phosgene gas. Lead coatings are not attacked by the gas. Also, in the adapter, the lead coating on the threads *acted as a gasket,* and that was found to be quite valuable." "If you have unions" (he proceeds), "and want a good, tight joint, it would be well to plate lead on the threads and then put on the caps of your unions. If forms a good gasket." This appears to be quite a useful suggestion. Chemical ware and works plant is now being, more and more, electro-plated with lead. L. Bradley[4] mentions, as an instance of the usefulness of lead deposition in this connection, a case where iron pails which were used for handling 30 per cent. sulphuric acid were found by him to have remained perfect after several months' usage. The applications just mentioned are interesting in themselves, but they are still more so in that they are, most of them, suggestive of others. It is, for instance, a matter of operation difficulty only that would prevent the inside surfaces of iron piping for use in chemical works being lead-plated by electro-deposition. It may be said in general that where there is a proposal to electro-deposit one metal on another, in order to protect that other from corrosion, it would always be as well to consider whether lead would not be the most useful and most economical metal to deposit. It will, indeed, seldom be found preferable to zinc; but there are few cases in which it would not be preferable to other common metals, and there are quite a number where lead, and lead alone, can be employed to the best advantage. There is, however, one matter which must not be neglected when a decision has to be reached, and it is a serious one. As A. G. Betts has pointed out,[1] commercial iron and steel often contain "imperfections in the shape of particles of grit or slag, some of which show on the surface and do not take the (lead) coating, with the result that there are pin-holes in the coatings at which corrosion starts." Emphasis is laid on this point here, because it has been neglected or ignored by the altogether too sanguine recommendations of several investigators who have done a little laboratory work in connection with electro-deposition, but have no considerable works experience. Much harm is done by such people to the true interests of electro-metallurgy.

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[1] W. Blum, *Trans. Am. Electrochem. Soc.*, 1919, vol. xxxvi. p. 265.

[2] *Trans. Am. Electrochem. Soc.*, 1919, vol. xxxv. p. 389.

[3] *Ibid.*, p. 399.

[4] *Ibid.*, p. 398.

PROPERTIES

Like other electro-deposited metals, lead has—often—different properties when deposited from one solution than it possesses when deposited from another. Current density and other conditions of deposition also influence the properties of the deposited metal. It may be light grey in colour, or it may be almost black, or, again, it may have almost any shade of colour intermediate between the two. The metal may be deposited as a dense sheet or as loosely adherent (skeleton) crystals, which, at times, will grow individually so as to stretch across the bath from cathode to anode and cause a short circuit. It may, again, be deposited as "sponge," similar in aspect to zinc "sponge." The deposit is sometimes hard and brittle, sometimes soft and malleable. In this respect the composition of the bath is of great importance; for it is not uncommon to find that, though two deposits formed in different baths, but under the same current and other deposition conditions, may look equally close-grained and smooth, one is brittle, while the other is malleable. The difference of composition may be no more than a difference of the "addition agent" which is present in the solutions.[2] The specific gravity of electrolytic lead, deposited from baths of different composition, has been found by Betts to vary between 11·20 and 11·39, being usually in the neighbourhood of 11·35.[3] The porosity of deposited lead varies also. W. Blum states that a thickness of 0·003 in. is sufficient to give an impermeable coating of lead, where the metal is deposited from the fluoborate bath, though he cautiously adds that if the deposit is to withstand corrosive liquids, deposits of 0·05 in., or more, may be necessary. The resistance offered by lead to corroding agents is well known; but it should be mentioned that H. Rodman[1] has stated that he found that though lead deposited from Betts' solution "is somewhat stiffer and, therefore, better from a mechanical point of view, it is apparently more liable to chemical and electro-chemical attack" than ordinary lead. "This characteristic," says Rodman, "renders it peculiarly unsuitable for Planté positive plates where the densest and most resistant lead is necessary." It does not, of course, follow that lead deposited from another solution than Betts' would be subject to the same defect.

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[1] *Trans. Am. Electrochem. Soc.*, vol. xxxvi. at p. 267.

[2] Cf. F. C. Mathers, *ibid.*, p. 266.

[3] W. Blum has given 11·3 as true specific gravity of lead deposited from fluoborate solutions.

LEAD-PLATING SOLUTIONS

Three lead-plating baths are available. Two of them have proved their worth in works practice; the third, which has only lately been worked out (and only partially so), is at present, one of the laboratory class. The first two baths are: (1) F. C. Mather's perchlorate bath,[2] and (2) A. G. Betts' silico-fluoride solution.[3] The third is a fluoborate solution, which, one must presume, is so called because it contains hydrofluoric and boric acids.[4] That, at any rate, is the only reason one can imagine for the name: certainly, the "inventors" nowhere show that the bath consists essentially of fluoborate, and it is, indeed, very doubtful if they know that it does.[5] The author does not consider this third bath to be sufficiently established to render its adoption (on any large scale) in works practice desirable at present. In so far as laboratory knowledge is concerned, it carries one little further than the work of previous investigators—work which appears to have been neglected by Blum and those working with him. All three baths have this characteristic in common—they all contain an organic addition agent. In this respect they resemble every other lead-plating bath from which a dense, smooth deposit is obtainable. Unless some substance, such as glue, peptone, clove oil, or the like, is present in a lead-plating solution, a useful deposit of lead cannot be obtained. Another common characteristic of most, if not all, useful lead-plating baths is that they contain free acid. The acid employed varies from bath to bath, but it is usually a member of the class known as "strong" acids, one, that is to say, that is well ionized in solution.[6] The fact that these two kinds of constituents are always, or nearly always, present in good lead-plating baths is an important one for those to note who desire to make up a bath for themselves.

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[1] *Trans. Am. Electrochem. Soc.*, 1909, vol. xv. p. 433.

[2] *Ibid.*, 1910, vol. xvii. p. 261.

[3] A full account of Betts' work will be found in *Lead Refining by Electrolysis*, 1908. (J. Wiley & Sons, New York.)

[4] W. Blum (and co-workers), *op. cit.*, pp. 247 and 248.

[5] See W. Blum, *Trans. Am. Electrochem. Soc.*, 1921, *sub* "The Use of Fluorides in Solutions for Nickel Deposition," and W. E. Hughes, "Recent Progress in Nickel-plating," *Electrician*, May 13, 1921.

[6] Cf. A. G. Betts, *Trans. Am. Electrochem. Soc.*, 1910, vol. xvii. p. 272.

MATHERS' PERCHLORATE BATH

(a) *Composition*

The composition that can be employed is evidently variable, since Mathers himself has recommended more than one, and the author has used, with equally good results, a bath of a composition different, as regards quantities, from any given by Mathers, though essentially the same as his perchlorate solution. Mathers gives as the compositions of two baths employed by him[1]: (i) 4·5 per cent. perchloric acid, 5·4 per cent. lead, and 0·05 per cent. peptone; and (ii) 6·1 per cent. acid, 7·13 per cent. lead, and 0·05 per cent. peptone. In a later paper,[2] Mathers states that lead *acetate* can replace lead perchlorate, and ammonium (or sodium) perchlorate and glue can be used in place of the acid and peptone. Still later,[3] Mathers has stated that "clove oil in the perchlorate bath gives a splendid, solid, smooth, finely crystalline deposit." The composition of a bath that has been successfully used by the author is as follows: 6 lb. lead perchlorate, 3 lb. perchloric acid (sp. gr. 1·250), 1 oz. peptone, and 12 gals. of water. It should be noted particularly that lead acetate can be used in place of the perchlorate, the other components remaining the same. This fact lessens the original cost of the bath; and the author has found that the substitution in no way interferes with the smooth working of the bath or causes any deterioration in the good qualities of the lead deposit. In addition to variability, the bath possesses the attribute of simplicity. There are three components only; and, if lead perchlorate is used, only, at most—apart from possible complex ions—three ions, namely, the lead and hydrogen (both of them cations), and the perchloranion. The function of each constituent is fairly clear. The lead salt supplies the metal; the perchloric acid (or ammonium or sodium perchlorate, where either of these is used) acts as a "conducting salt," and, as well, as an agent whereby the grain-size of the deposit is cut down or diminished; and the peptone as an "addition agent," which enables a smooth, dense deposit to be obtained from baths that, without it, would yield only deposits formed of loosely-packed and, often, large grains.[4] The bath conducts well. The anode and cathode efficiencies are very close to 100 per cent.[5] The bath is stable—does not change, that is to say, in composition on standing or with use: its composition remains, within working limits, constant. Mathers says (*op. cit.*, Note 20): "The perchlorate baths, which had been used for months, did not give any test for chlorides with silver nitrate. This shows that there is no loss of perchloric acid by slight reduction." Mathers has also determined that the loss of acid amounts to only 0·4 lb. per ton of lead deposited. The author would prefer to use the term "deficiency" rather than "loss" (of acid): it is very probably due to the bath as a whole becoming, in course of usage, less concentrated in consequence of the removal of solution on the plated articles and the introduction of water on the articles when suspended in the bath for plating. The deficiency can, of course, be easily made up from time to time by additions of acid, when this is seen to be necessary; the necessity is evident from the increase of voltage necessary to work the bath, from considerable variations in the thickness of the deposit over the surface of the articles (including absence or thinness of deposit in hollow parts of the surface), and from "current marks" in the surface of the deposit itself. Addition agent is carried over into and included in the deposited metal; that is an easily demonstrable fact. When the amount of this present diminishes below a certain necessary minimum,[1] the deposit becomes obviously crystalline, and less dense and smooth; but an addition of a small amount of the addition agent restores the deposit to its former consistence. Mathers says: "The peptone is gradually used up, and after about four days, a quantity equal to the original amount should be added." The author found that rather less was required. Those desirous of depositing lead are urged to obtain and consult Mathers' original paper: "Electro-deposition of Lead from Perchlorate Baths." It is to be found in the *Transactions of the American Electrochemical Society*, 1910, vol. xvii.

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[1] *Trans. Am. Electrochem. Soc.*, 1910, vol. xvii. p. 268.

[2] *Ibid.*, 1913, vol. xxiv. p. 315.

[3] *Ibid.*, 1919, vol. xxxvi. p. 266.

[4] What has been said in regard to the action (or function) of "addition agents" in Chapter VII. (Zinc), applies here also.

[5] *Trans. Am. Electrochem. Soc.*, 1910, vol. xvii. p. 265.

(b) *Working Conditions*

Mathers states that a *current density* of 18 to 20 amp./ft.^{2} may be used; but it is suggested, as the outcome of experience, that 10 amp./ft.^{2} is a good current density to employ for continuous deposition. The bath is worked at the ordinary *temperature*—60° to 70° Fahr. *Anodes:* These should be of good sheet lead. The anode surface should be large: a thickness of one-tenth of an inch is sufficient.

(c) *Operation*

No special rules are necessary to operate the bath. As in all plating, care should be taken to "strike" the articles quickly. In the case of articles made of iron and steel, it has been found advisable to coat them lightly with copper in a cyanide bath (and then swill them well in running water) before suspending them in the lead-plating solution. This ensures adhesion. The anodes will appear crystalline after the bath has been working for some little time. This is as it should be. If the anodes become covered with slime, then either they are impure, or the bath contains too little free acid and more must be added, little by little. As above indicated, if the *deposit* becomes visibly crystalline, more peptone is necessary. Mathers states that clove oil gives an even better deposit than peptone; but the author's experience is with the latter, and he can affirm that excellent results are obtained with that substance (peptone) as addition agent.

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[1] Cf. R. Marc, *Zeit. f. Elektrochem.*, 1913, vol. xix. p. 431.

(*d*) *Deposit*

The deposit obtained from Mathers' bath has a light grey colour. Deposits up to 0·024 in. can easily be obtained, possessing a surface that is very smooth. The metal appears to the eye to be structureless; but under the microscope it has a structure that is of great interest. This subject has been investigated by the author.[1] The deposited lead is malleable and ductile, and these, as indicated above, are important properties. At the same time, it is doubtful whether the deposit is ever chemically pure. Every sample tested by the author has been found to contain organic matter (derived from the peptone, most probably); its presence can be made a matter of ocular demonstration. The total amount of impurity does not, however, amount to more than some small fraction of 1 per cent., and there is very little (if any) likelihood of the small amount of impurity present being any detriment to the lead deposited for protective purposes. For instance, some samples of steel tube which were plated seven years ago and of which no special care has been taken are entirely free from rust to-day, so far as can be seen with a hand lens. If the deposit should at any time during its formation appear to the eye to be crystalline, more peptone must be added to the solution.

BETTS' FLUOSILICATE SOLUTION [2]

PRELIMINARY REMARKS

This bath was patented and first described in 1901. From that time it has become more and more used as a means of *refining* lead. It was, indeed, the only one, of practical use for that purpose, that was known until Mathers published his work. The solution has been closely investigated by H. Senn,[3] whose conclusions, as an independent investigator, are important. Stated generally, they are as follows: (i) Lead can be electrolytically refined in hydrofluosilicic acid solution, plates of coherent metal being obtained. (ii) Addition of gelatine to the electrolyte hinders the formation of individual crystals or stars of crystals. 0·1 gm./lit. is a suitable quantity of gelatine to use; the use of a larger amount is needless, as the beneficial influence on the deposit is not increased by the excess. (iii) The conditions for good deposits are: *Composition*: hydrofluosilicic acid, about 11 per cent.; metal content, 4 to 8 per cent.; gelatin 0·1 gm./lit. *Current density*, 0·5 to 1 amp./ft.^{2} In Senn's opinion, the metal is present as a constituent of lead silicofluoride. To make his solution, he diluted 33 per cent. hydrofluosilicic acid solution to 20° Bé., and carefully neutralized any sulphuric or hydrofluoric acids present with lead carbonate. The solution was then treated with 128·3 grms. of lead carbonate per litre, in order to obtain a solution containing 100 grms. of lead (metal) per litre. (iv) Senn concluded that to employ a more dilute solution than that just described, or a greater current density than that mentioned, proved harmful to the deposit. He obtained deposits 2 mm. thick.

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[1] *Jour. Phys. Chem.*, 1922, vol. xxvi. p. 316.

[2] Amer. Pat. No. 679,824 (1901). A somewhat later patent, No. 713,277 (1902), contains some further particulars. This patent seems to be in all respects the same as No. 713,278 of the same year (1902). *Vide* also *Electrochem. and Met. Indus.*. 1903. vol. i. p. 47.

[3] *Zeit. f. Elektrochem.*, 1905, vol. xi. p. 229.

It may be added that M. Schlötter says[1] that "using a solution containing gelatine, the current density can be raised to 2·5 amp./ft.^{2}, if the concentration of the electrolyte be 22° Bé., without outgrowths being formed." This, however, only applies to plating purposes as distinct from refining. The present author has done a considerable amount of work with Betts' solution and has obtained some good deposits from it; but two chief difficulties have been experienced, namely (i) those of a practical kind, which were met with when making up a bath of any considerable quantity—80 or 100 gals. or more; and (ii) those arising from the silica which was found to separate during the working of the solution or even when it remained unemployed. It was found that, at times, the silica interfered with the formation of a smooth reguline deposit, and even hindered the free passage of the current.

The opinions and experiences of some independent workers with the Betts solution have been given in the foregoing, and, incidentally, details of composition and working conditions have been stated. It will, however, be advisable to follow the course taken in former chapters in connection with the electro-deposition of iron, nickel, and zinc, and consider the Betts solution in relation to each of the subject matters mentioned. In the present instance, the details given will be, for the most part, those given by the inventor of the bath himself.

(a) *Composition*

Curiously enough, Betts does not state in the 1902 patent the composition of the solution he used. He says only: "To carry out my invention, I employ any suitable electrolyte—such as, for example, a solution of a lead salt of a fluorin acid. To the electrolyte is added a quantity of a reducing agent, which I have found materially improves the deposited lead. Among the substances which I have found available for such purpose are gelatine, pyrogallol . . ." Nor is a solution of definite composition recommended in what appears to be the original patent of 1901.[2] But it is stated in this that: "The relative amounts of lead fluosilicate and fluosilicic acid in the solution may vary according to the amount of work required to be accomplished by a given expenditure of power. 15 per cent. of lead fluosilicate in the solution will be sufficient for all strengths of current up to the practical limit. When for economical reasons it is desirable to have a minimum electrical resistance in the solution, the proportion of fluosilicic acid only should be increased, as the acid conducts better than the salt." In other words, Betts claims that the proportions of the ingredients are variable, and that they may be varied according to the end required. Such variability is always an asset in a plating solution. In the description given by Betts of the process in operation at the Canadian Smelting Works at Trail, British

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[1] *Galvanostegie*, 1910, Teil 1, p. 20.

[2] That is, No. 679,824.

Columbia,[1] the method of preparing the solution is too complicated for adoption in plating-shop practice. But in a later paper by Betts himself and E. F. Kern,[2] results obtained from two electrolytes are given, namely (i) 13·5 per cent. lead fluosilicate ($PbSiF_6$) and 6·5 per cent. *free* hydrofluosilicic acid (H_2SiF_6), and (ii) 8·5 per cent. of the lead salt and 2·5 per cent. of the free acid. The advantage of the more concentrated electrolyte is that, with it, higher current densities can be used.[3] The amount of gelatin used was, in both cases, 1 grm. to 2000 c.c. of solution, which equals (approximately) 2½ grms. per gal. Since solutions of the foregoing compositions were employed for coulometer work, one may assume that they satisfy all the needs of an ordinary plating bath. As a fact, the author has used solutions based on the above figures, namely, a bath having the composition 131·5 grms. lead fluosilicate, 61·5 grms. free acid, 0·5 grm. gelatin, and 1 lit. water, and obtained excellent deposits from it.

(*b*) *Working Conditions*

These are given by Betts in the patent specifications of 1901 and 1902. They are as follows : *Current density*, 10 to 20 amp./ft.^{2} (8 to 16 amp./ft.^{2} were used in the coulometer work); *Temperature*, ordinary ; and *Anodes*, a good quality of refined lead.

(*c*) *Operation*

The Betts solution has obtained extensive employment as a means for refining lead. The author is informed by the management of the Consolidated and Mining Company of Trail, British Columbia, that lead-refining by the Betts process is being carried on at Trail. " The plant installed here was the first of its kind built anywhere, though there are several others operating in the United States now." The plant has, at present, an output capacity of 110 tons of refined lead per day. It would seem, therefore, that the operation of the bath for refining purposes is a straightforward practical proposition. Nevertheless, the author has not found the solution easy to control as a plating bath. It may be that there are some details of practice to be observed in working the bath which are unknown to him, and the observance of which enable the good deposits, which can be, without doubt, obtained from the solution, to be regularly and consistently produced. It may be that the bath is one of that type that it is necessary to become thoroughly familiar with, as regards its working, before the best results are to be got from it in works practice.[4] However this may be, the operation of the fluosilicate bath is certainly more difficult than is that of the perchlorate. Not only does the gelatine become gradually used up and, hence, have to be replaced, but, as has been already stated and as is again insisted upon, it is found that colloidal silica separates in the solution, especially if the solution be allowed to remain unused for any considerable length of time. Such, at least, is the author's experience, and H. Senn mentions the same fault.[1] As a consequence of separation of silica, the anodes may become "clogged" by deposits of it upon them; such deposits will diminish the conductance of the solution as a whole, and they will, further, lessen the area of free anode surface. Another consequence is that some of the silica, floating about in the solution, will settle upon the cathodes and become incorporated in the deposits, thereby changing their physical properties. Another matter connected with the operation of Betts, bath is this—the constancy and uniformity of the composition of the bath in action are certainly not equal to those of the perchlorate bath, and this becomes a source of difficulty in a plating shop. The limits of working are, however, wide, which is always an advantage in a solution. A too high current density is indicated by the deposit assuming a silvery-white appearance, and excessive current density has the effect also of making the deposit harder and more brittle.[2] The anodes appear to dissolve well, and this, again, is a good point. The sufficiency of the gelatin content can be known from the microscopic aspect of the deposit. It is stated by Betts and Kern [3] that "With age and by use the gelatine slowly loses its reducing property. The appearance of the deposit indicates when more gelatine is needed, so that as long as the deposit forms smooth and non-crystalline, none need be added. The gelatine is added by dissolving a small quantity in hot water and adding it directly to the electrolyte. The moment it is added the crystallization of the lead is prevented." This passage from Betts and Kern is cited in full with a view to pointing out—especially—that the practice of adding a substance directly to a plating solution and in a haphazard quantity, is a thoroughly bad one. It is a practice which often brings about serious difficulties. The method described in Chapter IV. should always be adopted. Moreover, it is not accurate to say that the moment the gelatine is added the crystallization is prevented. As has been stated before,[4] the effect of an addition to a plating bath (especially one of 200 or 300 gals. in amount) always requires time to show itself. It is because workers will not remember this fact that, because of addition of excessive quantity, a medicine becomes a poison. Not once nor twice only, in the author's experience, has failure to grasp the importance of this fact been found to be responsible for serious plating troubles in the shop. In one instance a bath of 500 gals. of nickel solution had to be thrown away as a consequence.

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[1] *Electrochem. and Met. Indus.*, 1903, vol. i. p. 407.

[2] " The Lead Voltameter," *Trans. Am. Electrochem. Soc.*, 1904, vol. vi. p. 67.

[3] Betts and Kern, *op. cit.*, p. 78.

[4] There are many such baths. A man accustomed to silver-plating only would probably meet many troubles in working a brass-plating solution or, even, some tin-plating baths.

(*d*) *Deposit*

The deposit from the Betts bath is smooth and dense, light grey in colour, and, under the best conditions, free from outgrowths and nodules. It is, to the eye, non-crystalline. As already stated, if it is seen to become crystalline during deposition, more gelatine must be added. Betts and Kern[1] say that the deposit will always remain non-crystalline in appearance so long as the solution contains about 1 part of gelatin by weight in 2000 to 4000 parts of solution.

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[1] *Op. cit.*, p. 245, Result 5.

[2] Cf. Amer. Pat. No. 713,277 or No. 713,278.

[3] *Op. cit.*

[4] Chapter IV., *sub nom.* "The Upkeep of the Solution."

MICRO-STRUCTURE

Very little indeed is known about the micro-structure of electro-deposited lead. While considerable attention has been paid of late to the structures to be found in other deposited metals, that of lead has remained uninvestigated. One reason for this may be that the preparation of polished and etched sections of the metal for examination under the microscope is difficult. In fact, it is not too much to say that no general method of polishing and etching lead, whether electro-deposited or other, has, as yet, been developed. Another difficulty met with consists in the deposition of the metal in a form that will permit of polishing and etching at all. Unless addition agents are employed, dense, coherent deposits cannot, by present-day methods, be obtained—the deposit consists of a mass of loosely adherent skeleton crystals. On the other hand, if addition agents are used and a dense, homogeneous deposit formed, then the structure is so minute that the preparation of a polished and etched section becomes a process of still greater difficulty. Moreover, variations of crystal (grain) size with variations in the conditions of deposition appear to be less marked when addition agents are employed. That is a fact of note for its own sake. One line of attack that has yielded results of some promise consists in omitting the polishing operation altogether and etching the unpolished surface of the deposit by electrolytic means. A photograph of the unpolished, but etched surface of ordinary sheet-lead is shown in a contribution from the present author to the discussion on a paper on "The Electrolytic Etching of Metals," read by F. Adcock before the Institute of Metals.[2] The grain structure is well seen in the micrograph. Application of the method has been made to electro-deposited lead also; and observation of the etched surface of the metal with the microscope discloses a structure of great interest, but one which it is, at present, difficult to interpret.

The study of the micro-structure of electro-deposited lead is, though difficult, one which will, almost certainly, yield information of very great interest, and the results of it would, it is believed, be such as could, many of them, be put to good use in the workshops. There is here an almost untouched field of research.

TESTING

Many of the tests applicable to zinc deposits can be made to ascertain the value of deposited lead. Its value will, in most cases, be directly proportional to its covering power, by which is meant its power or capacity to cover up the underlying metal so as to prevent access to it of moist air or other corroding agents. The deposited lead functions in just the same way as does a paint or varnish. Hence, porosity of the lead coating will be a great detriment, and tests should be directed to determining this.[1] A simple test for pin-holes, cracks, and other discontinuities in the deposited metal—a test particularly applicable to metals such as lead, which are electro-negative to iron—is the following: Immerse the sample in a 1 per cent. solution of sodium ferricyanide in 2 per cent. sulphuric acid. If a blue precipitate appears at any part of the surface, a hole (or crack) in the surface is indicated.[2] The Bureau of Standards, Washington, states that acetic acid can be used for sulphuric, but that, in such case, the action is slower.[3]

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[1] *Op. cit.*

[2] *Jour. Inst. Metals*, 1921, No. 2, vol. xxvi. p. 361.

REFERENCES

W. E. Hughes.—"Studies on the Electro-deposition of Lead from Mather's Perchlorate Bath. I. The Structure of the Deposit," *Jour. Phys. Chem.*, 1922, vol. xxvi. p. 316.

Note.—An interesting criticism of the foregoing chapter has recently appeared in the *Zeit. f. Metallkunde*, 1922, vol. xiv. p. 210. Dr. Breuning is its author.

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[1] See Chapter VII., Zinc.

[2] The author has used this test for many years past in connection with nickel-plated iron and steel goods, and found it very reliable.

[3] *Bureau of Standards*, Circular No. 80, 1919.

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CHAPTER IX

TIN AND CHROMIUM

THE electro-deposition of tin is of considerable importance to engineers; but a mistaken idea that seems prevalent in regard to it needs to be pointed out. Just as nickel-plating is supposed by some people to prevent corrosion or rusting of the iron or steel underlying it, so is tin-plating. H. Altpeter[1] points out the falsity of this idea. He states that, while zinc serves both to protect and to improve the look of the iron or steel goods on which it is deposited, tin serves only the latter purpose. This, however, is too extreme a view, for a deposit of tin will certainly in some measure protect the iron or steel; but it must always be borne in mind that, in so far as tin affords any protection, it does so for the same reason as nickel does. It is, indeed, more effective—as a rule—than nickel, because it more completely covers the iron or steel on which it is deposited. The solutions used for tin-plating are, usually, much better conductors than nickel-plating baths, and they "throw"[2] into the hollows and crevices of the surfaces of the objects to be plated much better than do nickel-plating solutions. Hence the covering of tin over the iron or steel is much more nearly continuous than that of nickel, and thus there are fewer points of attack for the agents of corrosion to work at. But tin, like lead and nickel, has no inherent property to assist it to protect iron: like these metals, tin is electro-negative to iron, and it will only protect iron or steel in places where it *completely* covers it, and so prevents the access of moist air. Tin is, however, more resistant than zinc to fumes and gases that may be present in the atmosphere, but it is less resistant than lead or nickel. It may be said, in general, that the order of value of these metals as protectors of iron and steel from corrosion is: zinc, lead, tin, nickel, zinc being the most efficient, nickel the least.[3]

USES AND APPLICATIONS

The uses to which the process of tin deposition can be put are not so well known as they should be. It can be applied to tin-plating the flat trays and moulds used in chocolate factories and in works in which articles of diet, such as jellies and the like, are made. In these cases the moulds are, after being "electro-tinned," scratch-brushed, "quicked" in a solution of a salt of mercury,[1] and again scratch-brushed. The result is a bright surface. The purpose of the "quicking" is to prevent the chocolate or jelly from adhering to the mould on cooling, and thus enable the cakes of these goods to be separated from the moulds without fracture and with a clean surface. Biscuit manufacturers use the tin-deposition process to renovate the biscuit boxes (of tinned iron) that have been returned to the factory after circulation. Another use, for a purpose similar to that last mentioned, is that of re-tinning by electrolysis the pots and pans used for culinary purposes. If such articles are well cleaned, and then electro-tinned and scratch-brushed, they present quite a good—indeed, almost new—appearance. Several gasworks throughout the country seemed inclined, in pre-war days, to encourage this method of renovation. It would certainly "pay" at the present time, and there would probably be less difficulty now in overcoming that prejudice and ultra-conservatism which has always opposed the progress of electrolytic methods in this country. Electro-tinning has been, and is still, used to deposit tin on such classes of goods as lamps and lamp fittings, gas brackets, buckles, and the like. Fenders, bedsteads, fire-screens, and other metal furnishings are often so treated.[2] The object in these cases is to deposit a metal on the base metal—iron, brass, or other—that will be cheaper than silver and yet can be "oxidized," so as to appear like "oxidized" silver. A skilful metal colourer or bronzer can produce some very beautiful relief effects by this method, and it requires very close inspection to distinguish the "finish" from that of "oxidized" silver.[3] The use of tin for silver has at least one advantage in respect to the finished article: the tin will not tarnish as easily as will silver, if the lacquer should wear off.[4]

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[1] *Stahl u. Eisen,* 1916, vol. xxxvi. p. 780.

[2] This expression—"to throw"—is a term frequently heard in the plating shop. It is used of both solutions and deposits. "A solution does not throw well," means that it is difficult to plate with it the interiors of holes or cracks in objects.

[3] Cf. W. Lange, *Zeit. f. Metallkunde,* 1921, vol. xiii. p. 267.

PROPERTIES

Electro-deposited tin is, usually, of a dull white colour, even though deposited from a solution containing a colloid—for instance, gelatine.[5] This fact has undoubtedly militated against the development of the electro-tinning process. As W. Pfanhauser says:[6] "It has so far proved impossible to produce, electrolytically, a tin deposit which can be taken out of the bath in a *bright* condition." It is always necessary to scratchbrush the deposit, if one wishes to secure a bright surface similar to that produced in the "pot process"; and this necessity has often (in the author's experience) prevented the adoption of the electrolytic method. Electro-deposited tin is soft and malleable. After deposition has continued for half an hour or so, the deposit can be seen to become more and more crystalline; and if deposition be continued over any considerable length of time, the deposit is apt to become either spongy or dendritic. When thick deposits are required for any purpose, a colloid must be added to the solution. Deposits up to 0·02 in. thick, formed in such baths, have been found by the author to retain the ductility and softness characteristic of tin; but whether thick deposits will do so or not depends upon both the composition of the solution *and* the particular colloid used in it.

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[1] A suitable "quick" is made as follows: Dissolve 5 to 10 grms. of cyanide of mercury or of mercuric chloride (corrosive sublimate), and double that quantity of potassium cyanide in a little water, and make up the volume to 1 litre. (A. Brochet, *Manuel pratique de galvanoplastie*, 1908, p. 140; Baillière et fils, Paris.) *Mem.*: 28·35 grms. = 1 oz., and 4·536 litres = 1 gallon.

[2] The process of "oxidizing" tin requires considerable skill. Any one interested will find information in an excellent book by G. Buchner, entitled *Die Metallfarbung*, 1906, pp. 109 et seq., or in almost any volume of the *Brass World*. (Bridgeport, Conn., U.S.A.)

[3] The term "oxidize" is a misnomer. *Vide* Chapter I., p. 7.

[4] All "oxidized" goods must be lacquered.

[5] Cf. nickel and copper, which are usually bright when deposited from baths containing gelatine.

[6] *Galvanotecknik*, 1910, p. 60.

TIN-PLATING BATHS

A large number of tin-plating baths have been recommended in text-books and patent specifications. Most of them are worthless. The type of solution that has been most employed is one proposed by Elsner,[1] and based upon the protochloride of tin dissolved in caustic soda or caustic potash; a solution of this type will serve almost any purpose a tin-plating solution is required to serve. It may be mentioned here that the required thickness of a tin deposit seldom exceeds a very small fraction of a thousandth of an inch. Such a thickness as is obtained in some thirty or forty minutes from a bath of the type mentioned is usually considered sufficient. Deposits of the order of thickness here referred to are usually smooth and, apparently, structureless. They have not had time to appear crystalline to the eye, or to develop "trees." If, however, a really thick deposit is required, a colloid must be used, and it may be advisable to use a bath of the acid type—one, for instance, containing oxalates and oxalic acid (*vide infra*),[2] or phosphates and phosphoric acid. Both types of solution will be considered, but particular attention will be paid to the alkaline type, since that is, for practical purposes in the plating-shop (as distinct from the refinery), much the more important.

THE ALKALINE SOLUTION

(*a*) *Composition*

The solution recommended is one composed of ½-lb. of caustic soda, 1 lb. of protochloride of tin ("tin salts" as it is called in the trade), and 1 gal. of water. 1 oz. per gallon of potassium cyanide may be added, but for many purposes the addition of cyanide is unnecessary. The solution should be made by first dissolving up the caustic soda and then adding (a little at a time) the tin salt to the hot soda solution, stirring well and continuously while making each addition. If cyanide is to be used, the solution should be allowed to cool before the cyanide (separately dissolved in water) is added. Caustic potash may be substituted for caustic soda, but such substitution will add to the cost of the solution without adding to its efficiency. The proportions of the components need be only approximately those given. Almost every text-book has its own proportions.[1] Indeed, workshop experience shows that wide limits are allowable; but the author has always found the proportions given above to make a solution which, under the conditions to be mentioned, will yield good results. A bath with two or three components, namely, the "tin salts,"[2] which contains the metal to be deposited, caustic alkali to act as a *conducting salt*, and help to dissolve tin into the solution from the anodes, and (possibly) cyanide, which helps to keep the anodes clean and free from slimes on their surfaces, would seem to conform to the requirement of simplicity.[3] It so happens, however, that these three substances give rise in solution to complex compounds, as explained below.

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[1] *Vide* G. Langbein, *Electro-deposition of Metals* (trans. W. T. Brannt), 1909, p. 440.

[2] And cf. the *Brass World*, 1918, vol. xiv. p. 51.

(*b*) *Reactions*

A bath of the type given is essentially a solution of sodium stannite,[4] which is the compound formed when caustic soda and stannous chloride ("tin salts") react with one another chemically. The chemist represents the reaction by the equation:

$$\begin{array}{ccccccc} 2NaOH & + & SnCl_2 & \rightleftarrows & (NaO)_2Sn & + & 2HCl \\ \text{(caustic soda)} & & \text{(stannous chloride)} & & \text{(sodium stannite)} & & \text{(hydrochloric acid)} \end{array}$$

The arrows used in the place of the usual, but often incorrect, sign of equality, denote that the reaction may proceed either way—from right to left, or left to right—according to conditions. It is what is called in chemistry a "reversible" reaction:[5] it is, moreover, not complete in either direction, but proceeds to a certain extent only, and thus the solution contains some of the original components as well as some of their products of interaction. And in addition to the four substances shown in the equation, there may be potassium cyanide, if this is added, and, almost certainly, carbonate, this being an impurity found in all commercial caustic alkalis. It will thus be seen that the simplicity of the bath, as judged by the number of components from which it has been made, is apparent only and not real. It is necessary, moreover, to remember that the composition of the solution will soon become still more complicated by reason of the alteration of the substances present by (i) the oxygen and carbonic acid gas contained in the air, and (ii) the reactions brought about at the electrodes in consequence of electrolysis. In this respect the solution is like *all* alkaline baths, whether the silver-plating bath, brass-plating bath, or other. No alkaline bath can be stable, or, in other words, immune from chemical alteration or change.

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[1] Cf. H. Stockmeier, *Handb. d. Galvanostegie*, 1899, p. 116; G. Langbein, *loc. cit.*; and W. Pfanhauser, *op. cit.*, p. 604.

[2] The full chemical formula of "tin salts" is $SnCl_2, 2H_2O$.

[3] *Vide* Chapter IV. p. 35.

[4] Not *stannate*, as is sometimes said. *Vide* G. Senter, *Text-book of Inorganic Chemistry*, 1911, p. 480.

[5] J. W. Mellor, *Chemical Statics and Dynamics*, 1904, chap. iv. (Longmans.)

C. J. Wernlund[1] has turned a blind eye to the above-mentioned important matters in his recent enthusiastic advocacy of the use of cyanide solutions for the deposition of zinc, and this fact impoverishes the whole of his argument. Once more, for emphasis—*There is no such thing as a stable or, even, "fairly stable," alkaline plating solution*: ex natura rerum, *there cannot be.*

It will thus be seen that to endeavour to reduce such chaos to order would be waste of time. It is not worth while to try to visualize the happenings at the electrodes during the passing of the current.

In the case of the tin-plating solution, it would be foolish for the author to urge an operator to try to visualize the electrode reactions. He could not do so himself—no one could. The chemical reactions are not known, and the electrode reactions must depend upon these. All one can say is that tin may, in the result and in some degree, be deposited at the cathode, while tin will to some extent be dissolved at the anode. What the reactions are that result in deposition and solution respectively is not known. At the same time, insistence on the difficulty in the present instance is of use for a number of reasons. First, such insistence makes it the clearer how unsatisfactory the tin-plating solution in most general use is. It cannot be controlled in a scientific way. Second, it follows that there is need for research to discover some efficient solution that can be so controlled. Such research can be conducted by any intelligent plater during his daily work in the plating shop. And, third, it is evident that alkaline solutions are not, and never can be, of the same utility as the means for continuous deposition as acid baths are. They are not and cannot be made stable; and to urge[2] the use of alkaline baths on the ground that "the cyanide plating solution requires less careful cleaning of the work than the sulphate solution," is no less than encouragement of slovenliness.

(c) *Working Conditions*

Different authors recommend different working conditions.[3] Those which the author and experienced platers working with him have found to be the best are: *Temperature*, 150° Fahr., or higher. *Current density*, as great as can be employed. *E.M.F.*, 3 to 4 volts, at a rod distance of 9 to 10 inches. *Specific gravity* should be maintained between 9° and 10° Bé. at the working temperature. *Anodes*, good cast metal only should be employed. *Agitation*, rod movement if possible.[4]

(d) *Operation*

The working limits of the bath are fairly wide and vary with the amounts and proportions of the components employed. This is one of the very few good points of the bath. As Pfanhauser says, if a deposit of more than a very small fraction of an inch is required, the goods must be removed, at intervals, from the bath, swilled, scratch-brushed, swilled again, and replaced. But, as a rule, a very thin deposit is all that is required in tin-plating. The author has always found that the best results are obtained if, and only if, the solution is maintained at a high working temperature. A better deposit is then obtained, and obtained in less time than at a low working temperature, since a higher current density can be used. As regards current density, it is not of much use to try to work by the ammeter. Experience soon shows the operator when his current density is too high: the deposit will become powdery and of a dirty colour. The edges and corners of the goods must be watched, since in these places the current density is highest, and there the effects will be first seen. Experience must, in fact, be the guide in working this bath. Supply of metal will be aided by suspending (in a basket) in the solution some granulated tin. The metal in that form presents a large surface for attack. The anodes should be as many in number as the rods will accommodate, and they should be removed from the bath when it is not at work. The following points may be noted: (i) Slow deposition indicates either low metal content or too high alkali content. (ii) The formation of a scum or layer of white or yellowish solid on the anodes indicates insufficiency of alkali. If, therefore, deposition is slow and the anodes clear, the addition of " tin salts " only is necessary. Since, in this, as in all other tin-plating solutions, the anode efficiency is poor, metal must be added in the combined form as salts. But, whatever is added, the rules before mentioned[1] should be scrupulously observed, and especially the rule that only such amounts of substances should be added as have been ascertained and are known to be necessary from trial on a small volume of solution taken from the bulk.

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[1] Vide *Trans. Am. Electrochem. Soc.*, 1921, vol. xl. p. 257.

[2] As does Wernlund, *op. cit.*, p. 364. And *vide* the author's remarks on the so-called "cleaning and plating solutions" (*Electrician*, Nov. 18, 1921).

[3] Cf., for instance, W. Pfanhauser, *op. cit.*, p. 604.

[4] *Brass World*, 1918, vol. xiv. p. 51.

THE ACID SOLUTION

The only acid bath that has been shown to be at all satisfactory for plating purposes is that devised by F. C. Mathers.[2] The purpose of this bath is to obtain thicker deposits of tin as the result of continuous deposition. This is not a frequent requirement. Mathers' bath would, of course, be serviceable for producing thin deposits,[3] but it would be too expensive in upkeep for that purpose, which, as has been said, is served, in most cases, quite well by the alkaline bath. The author's experience with Mathers' bath is, comparatively, limited, but it is sufficient to enable him to recommend it. Indeed, Professor Mathers' reputation for careful work is sufficient of itself. The following particulars are those given by Mathers:[4] (i) *Composition*, 5 per cent. stannous oxalate, 6 per cent. ammonium oxalate, 1½ per cent. oxalic acid, and ¼ per cent. peptone. The stannous oxalate may be made by precipitating stannous chloride (" tin salts ") with oxalic acid. (ii) *Working conditions.—Current density*, 4 amp./ft.^{2}, though rather more current may be used. *E.M.F.*, the average is ½ volt at about 2-in. rod distance. *Temperature*, ordinary. (iii) *Operation.* Lack of metal (tin) in the bath is shown by the deposit becoming dark, and an addition of stannous oxalate must be made. If the anodes become covered with insoluble material, they must be brushed till clean, and an addition of ammonium oxalate must be made to the solution. Finally, when the deposit shows projecting crystals, peptone must be added.

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[1] In Chapter IV.

[2] *Trans. Amer. Electrochem. Soc.*, 1916, vol. xxix. p. 411.

[3] Cf. G. A. Roush on Mathers' paper, p. 415.

[4] Cf. *Brass World*, *loc. cit.*: stannous oxalate, 6 oz.; ammonium oxalate, 6 oz.; peptone, ¼ oz.; water, 1 gal. E.M.F. (at 9-inch rod distance), 2–3 volts.

General Comments

The foregoing particulars are, as the author has found, sufficient to enable a worker to obtain good deposits of considerable thickness from Mathers' oxalate bath. But the solution is not by any means an entirely satisfactory one. The inventor himself points to some defects when he says[1]: "During electrolysis, a fine yellow precipitate forms in the bath and settles to the bottom as long as sufficient oxalic acid is present, but if the bath needs more oxalic acid, porous, crystalline salts form on the sides of the beaker and on the electrode connections at the surface of the liquid, and gradually climb upward. The addition of more oxalic acid stops this." Mathers does not say what the yellow precipitate is, but, most probably, it is a complex salt of tin;[2] and hence, even when the bath functions well, metal is precipitated from the solution as a constituent of a salt, and it is lost, therefore, to that extent to the cathode deposit. This is serious, since metal lost in this way has to be regained by the solution somehow; and the only way available is by addition of stannous oxalate, as the anodes do not supply metal sufficiently fast to compensate even for that removed by deposition at the cathode. Moreover, the presence of suspended matter in a solution is always a source of difficulty, because deposits formed in baths containing it are apt to be rough and also to contain such matter as inclusions.[3] Again, on p. 413, Mathers says: "In spite of these additions to the baths, they finally become so deteriorated that bright, solid deposits could no longer be obtained." This indicates that the bath is liable so to deteriorate in course of time that it becomes impossible to restore it; and this is an indication that control of the bath is far from satisfactory. This liability to deterioration is further referred to in a later paper by Mathers and W. H. Bell.[4] Mathers says of the type of bath considered in that paper, namely, the alkaline tin-plating bath, containing addition agents: "The great difficulty of these baths is their deterioration during operation or on standing.[5] A precipitate forms and the amount of stannous tin decreases until good deposits can no longer be obtained. This last cathode shows a deposit from the same bath after standing for three weeks—a bath from which one of the best deposits was obtained. This deposit is loose and entirely bad. *We found no method of preventing this deterioration.* We do not recommend this bath for tin-plating because of this deterioration." And later: "The regular addition of tin salts to this bath was equivalent to the preparation of a series of new baths. My idea of a good bath is one that maintains itself for a long time with only unimportant change." It is a fact that no entirely satisfactory bath has been found that will give good, smooth, and thick deposits of tin over long periods of time.[1] Research is, therefore, necessary for the discovery of one. Before, however, any such work is commenced, the results of previous investigators should be studied. It is to facilitate such studies that a number of references to researches on the electro-deposition of tin have been collected below.[2]

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[1] *Op. cit.*, p. 413.

[2] Cf. the yellow precipitate that is sometimes formed in A. Classen's oxalate solution for the electro-analysis of iron.

[3] *Vide* Fig. 1, which shows the effect of an inclusion of iron oxide upon the structure of an iron deposit. See also *Jour. Iron and Steel Inst.* (1920, No. 1), vol. ci. pp. 328 et seq., and Fig. D., Plate VI., Fig. A., Plate VII., and Fig. A., Plate VIII.

[4] *Trans. Am. Electrochem. Soc.*, 1920, vol. xxxviii. p. 135.

[5] The chemical process is: $6SnCl_2+2H_2O+O_2=2SnCl_4+4Sn(OH)Cl$. The so-called *basic* chloride, $Sn(OH)Cl$, is insoluble, and, therefore, is precipitated. Roscoe and Schorlemmer, *Treatise on Chemistry*, 1907, vol. ii. (Metals), p. 839.

ANODES

One great fault of tin-plating baths is that the anodes do not dissolve well, with or without the passing of the current. This is, no doubt, due in part to the component substances used in the solution; but it is also due in part to the anodes. There is little doubt that makers of tin anodes do not trouble themselves about the requirements of the plating shop: the anodes are cast under conditions that suit the convenience of the makers. The same remarks that have been made respecting nickel anodes[3] apply equally as much to tin anodes. If anodes of the right composition and constitution were made and used, it is more than probable that they would function better during electrolysis. Only research will disclose what the most suitable composition and constitution are; and it is the business of the electro-metallurgist to conduct such research and to tell the maker what he requires and ask him to supply it. The electro-metallurgist and plater will not solve their problem by blaming the manufacturers: they must help themselves, and that can be done only by research.

STRUCTURE

The internal structure of tin deposits has not been studied; but observations on the macroscopic appearance of them have, long ago, been recorded. It is well known that electrolysis of solutions of tin chloride produces skeleton crystals or "trees." In 1904, A. B. Sapojnikoff published a paper[1] in which he described them, after examination of them with the microscope. Still earlier, in 1877, O. Lehmann[2] had described the crystals, and accounted for their formation by assuming "that the phenomena of formation of crystals electrolytically are in line (*sich anreihen lassen*) with those of the formation of crystals in ordinary." The assumption seemed, he says in a later paper,[3] so bold that he followed the matter further, and the result of his investigations was that his assumption was supported. This hypothesis, namely, that the same laws of crystallization hold for the crystallization of deposited metal as govern the crystallization of other substances, has been more fully developed by the author, and applied to the case of electro-deposited iron.[4] In the absence of direct evidence of the internal structure of tin, this has to be inferred from the macroscopic aspect of the deposit; but, as one finds in the cases of copper, iron, and zinc (and also lead) that the two are related, the inference for the case of tin is not unjustified. Experiment shows that causes which produce certain effects on the macroscopic aspect of the other metals mentioned produce similar effects (in kind, though not always in degree) in the case of tin. For instance, the effects of addition agents, added to a tin-plating solution, are often similar to those produced in a lead-plating bath: in both cases, "treeing" is often prevented, the grain-size of the deposit is diminished, and a solid deposit formed. Again, Mathers notes that the crystalline structure of tin deposits from the oxalate bath "was more pronounced" when the working temperature was 50° C. than at lower temperatures. This means that the grain-size of the deposit increased with temperature: so does the grain-size of deposits of iron formed in the ferrous calcium chloride solution.[5] Other correspondences could be pointed out; but, when all is said, inference remains inference—it is not fact. Only research can decide whether, in fact, the factors of deposition (current density, temperature, and so on) have the same effects on the structure of tin deposits as they have on the structures of other deposited metals.

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[1] A possible exception is a bath M. Schlötter is said to have invented. The author has been unable to ascertain the composition of this bath.

[2] In addition to those in previous notes, the following are references to important papers: U.S. Pat., No. 921,943, and *Met. and Chem. Eng.*, 1909, vol. vii. p. 285; E. F. Kern, *Trans. Am. Electrochem. Soc.*, 1913, vol. xxiii. p. 199; F. C. Mathers and B. W. Cockrum, *ibid.*, 1914, vol. xxvi. p. 133; F. C. Mathers and B. W. Cockrum, *ibid.*, 1916, vol. xxix. p. 405; E. F. Kern, *ibid.*, 1918, vol. xxxiii. p. 155, and 1920, p. 187. See also W. O. Snelling, *Met. and Chem. Eng.*, 1910, vol. viii. p. 247; K. Elbs and H. Thümmel, *Zeit. f. Elektrochem.*, vol. x. p. 364; F. Förster and J. Yamasaki, *ibid.*, 1911, vol. xvii. p. 361; and E. Näf, *Diss. Dres.*, 1911.

[3] Chapter VI., *ante.*

CHROMIUM

The electro-deposition of the metal chromium has not yet become a workshop process. Its deposition has, however, been the subject of study by competent investigators, and many of the properties of the deposited metal have been ascertained. In the author's opinion, the results obtained fully justify G. J. Sargent's view that "Chromium-plating has commercial possibilities owing to its extreme resistance to corrosion by air, moisture, and many chemicals."[6] There are, too, other possibilities than those particularly indicated by Sargent. Chromium is a very electro-positive metal,[1] and may, therefore, be capable of affording protection to iron from rusting. Moreover, there is a possibility that a thin layer of chromium, deposited on iron, could be made to alloy with the iron by suitable methods of heat-treatment, in which case a chromium-iron surface layer would result and, possibly, a non-rusting ("stainless") surface be obtained. It is true that, as regards this last possibility, Professor Bancroft found that the two metals would not alloy below a temperature of 1200° C.; but he does not give any account of his work on the matter, and it may well be that his conclusions are not final. In view of the foregoing possibilities and the importance of their realization to engineers, the author believes it will be of use to consider the electro-deposition of chromium here; but the treatment of the subject will be different from that adopted when dealing with the deposition of other metals. The principal object in mind is to assist any one wishing to undertake research in connection with the deposition of chromium for one purpose or another. The method of treatment will, therefore, be as follows: Some typical researches to be found in the literature will, in the first place, be briefly summarized. The principal matters concerning the deposition of the metal upon which light is thrown by the investigations considered will, then, be pointed out; and, finally, the properties of electro-deposited chromium will be described.

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[1] *Journ. Russ. Phys.-Chem. Soc.*, 1904, vol. xxxvi. p. 334.
[2] *Zeit. f. Krystallog.*, 1877, vol. i. p. 453.
[3] *Ibid.*, 1890, vol. xvii. p. 272.
[4] *Electro-deposition of Iron*, published by H.M. Stationery Office.
[5] W. E. Hughes, *op. cit.*
[6] *Trans. Am. Electrochem. Soc.*, 1920, vol. xxxvii. p. 496.

LITERATURE

(*a*) *R. Bunsen's Work.*[2] The two most important results of Bunsen's experiments were that he showed that the two factors of deposition which have to be especially considered in connection with chromium are current density and the concentration of the electrolyte. Both must be great, if successful results are to be achieved.

(*b*) *The Placet-Bonnet Patents.*[3] These are referred to here, partly as being of historical interest, and partly because excellent deposits of chromium are said to have been obtained by the methods patented. The author's opinion of these methods is that they must be very difficult to carry out, and results as good, and probably better, can nowadays be obtained by simpler methods. W. Borchers says, somewhat caustically, after detailing the principal Placet-Bonnet process: "Any criticism of the above is obviously superfluous." At the same time, it must be stated that later investigators[4] have commented more favourably upon it.

(*c*) *B. Neumann's Account of G. Glaser's Experiments.*[5] Glaser investigated the effects of current density, concentration of electrolyte, and working temperature, respectively, upon the electro-deposition of chromium. He used the divided cell arrangement—an inner cell containing the solution of a chromium salt (called "the catholyte"),[1] and itself contained in an outer vessel which held a mineral acid or a solution of some salt (called "the anolyte"), in which the anode was suspended. Glaser's results may be summarized thus: (i) *Current density.* Using *chromium chloride* solution, containing 10 grms. of metal per lit., as catholyte, pure metal was obtained at 9·1 amp./dcm.^{2} (about 90 amp./ft.^{2}) with an efficiency of 38·4 per cent. Above that current density, pure metal was obtained, but it consisted of crystals more or less loosely adherent, and the efficiency was not increased. Using *chromium sulphate* as catholyte, the best conditions were, at ordinary temperature, 65 to 85 grms. of metal per lit. of solution, and 13 to 20 amp./dcm.^{2} (117 to 180 amp./ft.^{2}), which gave a yield of 84·6 per cent. (ii) *Concentration.* Using *chromium chloride*, the best concentration was found to be 158 grms./lit., giving an efficiency of 56·6 per cent. Above that concentration the deposit was powdery: below it the deposit was mixed with oxide, and at quite low concentrations (below about 70 grms./lit.) only oxide and gas (hydrogen) were obtained. Using *chromium sulphate*, similar changes were found to occur with concentration changes as occurred when chromium chloride was the catholyte. (iii) *Temperature*, good deposits were obtained up to 50° C. Above this, black powder was formed at the cathode. It was found, too, that increase of temperature from the ordinary only slightly increased the percentage yield. Neumann remarks: "As one sees, it is only between definite limits of concentration, current density, and temperature, that it is possible to obtain useful metal deposits."

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[1] W. Muthmann and F. Fraunberger found the potential of chromium, against a normal KCl solution. to be at least +0·63 volt. Vide *Sitzungsber. d. Bayr. Akad. v. Wissenschaft*, 1904, vol. xxxiv. p. 212.

[2] *Pogg. Ann.*, 1854, vol. xci. p. 619; *The Chemist*, 1854 (No. 11), p. 686. An account of Bunsen's work will be found in W. Borchers' *Electro-smelting and Refining* (trans. by W. M'Millan), 1904, p. 496 (Griffin).

[3] D.R.P., No. 66,099 (1890); Eng. Pats., No. 19,544 (1890), and Nos. 22,854, 22,855, and 22,856 (1891), and No. 6751 (1893); U.S. Pat., No. 526,114. See also *Compt. rend.*, 1892, vol. cxv. p. 945.

[4] *Vide* H. R. Carveth and collaborators, *infra.*

[5] *Zeit. f. Elektrochem.*, 1901, vol. vii. p. 656.

(*d*) *F. Salzer's Patents.*[2] The author has obtained only fair deposits of chromium from the solution and under the conditions recommended by Salzer. But, on the other hand, F. Förster[3] appears to have been more successful. His remarks are as follows: "Salzer has found that for the production of good cathode deposits of chromium, an electrolyte consisting of a mixture of chromic acid and chromium chloride, *together with a content of free sulphuric acid*, is suitable. The ratio of metal in these two forms should be as 4 : 3, or as 1 : 1." Förster states that he can confirm the fact that, with 2 to 5 amp./dcm.^{2} and 3 to 6 volts, one can obtain very hard, smooth and flexible deposits of chromium, which have a steel-grey colour and can be formed to any thickness.

(*e*) *G. J. Sargent's Researches.*[4] Between 1901 and 1920, the date of publication of Sargent's work, there were published the results obtained by a number of other workers. It is unnecessary to consider these in detail here, because they are referred to by Sargent in his paper, and, no doubt, formed a guide to him in his work. But they would have to be studied by any one about to undertake researches upon the deposition of chromium, and they are, therefore, collected in a note (*infra*),[1] together with references to sundry patents. Sargent worked with the usual single cell arrangement, and used copper cathodes thinly covered (by plating) with chromium, in order to avoid loss of copper[2] and platinum anodes. He has himself summarized his results as follows: "Very good deposits of chromium have been obtained from chromic acid solutions containing small amounts of chromium sulphate. The deposition of chromium is affected very markedly by the per cent. of chromic acid and chromium sulphate present, and by the temperature of the solution and the cathode current density used, *so that good results are obtained only by a careful control of these factors.* The thickness of chromium deposits obtainable depends on the current density, the lower the current density the thicker the deposit. The use of low temperatures makes it possible to obtain fair ampère-hour yields of chromium at comparatively low current densities. A deposit ½-in. (1¼ cms.) thick has been obtained from a plating solution containing 24·5 per cent. CrO_3 and 0·3 per cent. $Cr_2(SO_4)_3$,[3] at a temperature of 20° C. with a cathode current density of 10 ampères per sq. decimetre. A yield of 0·10 grm. of chromium per ampère-hour may be obtained under these conditions with a voltage of a little over 3 volts with an electrode distance of about 1 in. The 0·3 per cent. of $Cr_2(SO_4)_3$ is a very essential constituent of the plating solution, as without it no more than traces of chromium can be obtained under the conditions given."

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[1] The solution in the neighbourhood of cathode and anode, respectively, is often called *catholyte* and *anolyte*.

[2] Amer. Pat. No. 900,597 (1908), and D.R.P. Nos. 221,472 and 225,769 (1909).

[3] *Zeit. f. Elektrochem.*, 1909, p. 809.

[4] *Trans. Am. Electrochem. Soc.*, 1920, vol. xxxvii. p. 479.

COMMENTARY

The foregoing is but a very brief résumé of a few of the principal researches that have been published on the electro-deposition of chromium; but it will suffice for the object to be served here. It is essential that any one commencing research on the deposition of chromium should consult not only the papers that have been considered in the text, but also those referred to in the notes. Some principal matters upon which light has been thrown by those who have investigated the electro-deposition of chromium will now be briefly referred to.

1. The later researches on the deposition of chromium (of which Sargent's is typical) confirm all the earlier work (from Bunsen on) in these particulars: For successful work, a concentrated solution is neces-

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[1] J. Férée, *Bull. Soc. Chim.*, 1901 (3), vol. xxv. p. 617, also at p. 620. H. R. Garveth and W. R. Mott, *Jour. Phys. Chem.*, 1905, vol. ix. p. 231; and H. R. Garveth and B. E. Curry, *Jour. Phys. Chem.*, 1905, vol. ix. p. 353, and *Trans. Am. Electrochem. Soc.*, 1905, vol. vii. p. 115: both these are very important papers. M. le Blanc, *Trans. Am. Electrochem. Soc.*, 1906, vol. ix. p. 315: the discussion on this paper is controversial, but very instructive. M. le Blanc, *Die Darstellung des Chroms* (Knapp-Halle). The following should also be consulted: Geuther, *Lieb. Ann.*, 1856, vol. xcix. p. 314; *ibid.*, *Lieb. Ann.*, 1858, vol. cix. p. 129; Buff, *Lieb. Ann.*, 1857, vol. ci. p. 1, and 1858, vol. cx. p. 278; Paposogli, *Gazz. Chim. Ital.*, 1883, vol. xiii. p. 47; S. Cowper Coles, *Chem. News*, 1900, vol. lxxxi. p. 16; W. Borchers, *op. cit.*, and the Moller-Street Patents, Eng. Pat. No. 18,743 (1898); D.R.P. Nos. 104,793 and 105,647 (1898).

[2] The author also found when working with Salzer's solution, that copper cathodes were attacked unless quickly "struck," *i.e.*, quickly covered, with a deposit of chromium.

[3] $Cr_2(SO_4)$ is the chemical formula for chromic sulphate: chromous sulphate has the formula $CrSO_4 7H_2O$.

sary; high current density must be employed; low temperature is better than high temperature; and agitation is advisable. These facts support Förster's general statement,[1] to the effect that "the conditions favourable to the electrolytic separation of a more electro-positive metal from aqueous solution are, therefore, the employment of high current density and a quite concentrated, at most *weakly* acid, solution of simple salts of the metal in concern."

2. It is possible to obtain thick deposits of chromium easily, if work be conducted under proper conditions.

3. It is not necessary to work with the divided cell arrangement of the earlier workers; this would be inconvenient in ordinary plating-shop practice.

4. If the divided cell arrangement is used, solutions of chloride or sulphate can be employed alone as catholyte; if the ordinary plating arrangement is used, a mixed electrolyte seems advisable, one component being chromic acid.[2]

5. Very little endeavour seems to have been made to ascertain whether chromium anodes can be usefully employed. Carbon, lead, and platinum have usually been used hitherto. The anode side of the bath has, as is too often the case, been neglected.

6. Since an insoluble anode has been the type employed up to the present, metal (chromium) must be supplied to the solution by way of addition of metal-containing salts. Such means of supply is always a defect in a plating process, and it is, therefore, all the more necessary to study the anode side of chromium-plating baths.

PROPERTIES

The properties of electro-deposited chromium, like those of other deposited metals, vary with the conditions under which the metal is formed. The colour is usually grey, light or dark: it is sometimes tinged with blue. Neumann describes some of Glaser's samples as looking very much like steel, and J. Férée states that his deposits were silver-white in colour.[3] The metal may be hard or, comparatively, soft; and it is sometimes brittle. The author found samples from Salzer's bath to be very brittle. Its hardness is given by Sargent as 75 on the sclerescope, while Bancroft states that specimens he examined were "not very brittle and fairly hard, but, of course, it is not anything like as hard as chromium carbide." A sample before the author while writing is of a bluish-grey colour, and soft enough to be marked with the finger-nail. The purity of the metal is high. Neumann states that Glaser's metal was found to contain only 0·1 to 0·2 per cent. of iron; but he does not mention other impurities, such as chlorine, sulphate, and hydrogen, and other gases. The macroscopic aspect of the deposits may be bright (*glänzend*) and, apparently, structureless, or dull—also without apparent structure. But the deposited metal may have a visibly crystalline structure : it may be of fine or coarse crystal grain, and the crystals may be inter-adherent and form a compact mass of metal, or they may be loosely adherent and even dendritic. As is the case of tin, the macroscopic aspect of the deposit is important, because it is very probable that one can infer from it the internal structure of the metal, which, up to the present time, has not been studied. Sargent mentions[1] that electro-deposited chromium is practically unaffected by air, oxygen, or chlorine, at temperatures up to 300° C., and that it oxidizes at about the same rate as nickel, at a temperature of 1200° C. The author has found that chromium deposits will dissolve in dilute sulphuric acid and also in hydrochloric acid. Bunsen says[2] the metal is insoluble in boiling nitric acid, while Férée found[2] it to be insoluble in cold concentrated nitric acid, concentrated sulphuric, or concentrated potash solution. A not unimportant property of deposited chromium is its capacity to "occlude" gases : in this it resembles both nickel and iron. Garveth and Curry[2] state that the metal can occlude 250 times its own volume of hydrogen. This property of taking up, or "occluding" (as it is called), gases is important, because such occluded gas will almost certainly affect the properties of the metal.

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[1] *Elektrochemie wässer. Lösung*, 1905, p. 195. (Barth, Leipzig.)

[2] Cf. Salzer's patents and Sargent's results.

[3] Férée worked with solutions of potassium chromium chloride that contained 266·5 grms. of chromium chloride and 233 grms. of potassium chloride per litre. He employed the low current density of 14·4 ampères per square foot.—*Bull. Soc. Chim.*, 1901, Series 3, vol. xxv. p. 617.

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[1] *Op. cit.*, p. 495.

[2] *Op. cit.*

CHAPTER X

COPPER

MUCH has been written about the electro-deposition of copper, and a great number of patents have been filed. Nevertheless, it is true that, on the scientific side, there still remains much to learn, and, on the practical side, existing knowledge of the properties and structure of the deposited metal is by no means great. The former truth has lately been recalled by a paper read by T. R. Briggs before the 1921 autumn meeting at Lake Placid of the American Electro-chemical Society. Though an important one, this paper will not be considered here; it is of scientific rather than of practical interest, and is, perhaps, controversial. The latter truth must be clear to all who have studied the literature concerning the electro-deposition of copper. A certain amount of research work has been published with reference both to the properties and to the structure of the metal. But in very few cases has systematic work been carried out regarding either, and little has been done to connect up properties and micro-structure, and to show how these are inter-related. It is hoped that some assistance will be given here to those who really wish to perform their work with scientific understanding, and not merely by rule of thumb. The best practice in any branch of applied science is always that which is based upon knowledge of principles.

PROPERTIES AND APPLICATIONS

1. *Properties.* Electro-deposited copper varies in properties according to the conditions of deposition. It varies in colour from bronze to salmon pink. It may be ductile or brittle, soft or hard: it is almost always brittle and hard when deposited from solutions containing colloids, *e.g.*, gelatine. It may be obviously crystalline in varying degree, or, to the unaided eye, structureless, in microscopic aspect. The ideal of the plater is a deposit that is of a fine salmon-pink colour, so ductile that it can be bent backwards and forwards many times without splitting, and matt and smooth in aspect and without visible structure. The electrical and thermal conductivities of the metal are high; that is why it is so frequently used as the conducting material in electro-technical work and in aeroplane mechanisms.[1]

2. *Applications.* It is unnecessary to consider the applications of

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[1] Further information will be found in W. Borcher's *Electric Smelting and Refining*, 1904, pp. 184 et seq. (Griffin.)

copper deposition here. Something has already been said about them;[1] and the practical applications of the process that have been recently made are fully described in C. W. Denny's little book.[2]

COPPER-PLATING SOLUTIONS

The operator has one of two general objects in mind when engaged in the electro-deposition of copper. One of these requires only a thin deposit; the other necessitates a thick one, and one only to be acquired by continuous deposition over a considerable length of time.[3] In the former case, the object is usually to provide some other metal—iron, very often—with a coat of a metal (copper) which can, by a simple process, be treated so as to make the iron article more presentable. Something has already been said about this object of copper deposition;[4] and it has been indicated that to carry it out, the alkaline or cyanide of copper bath is usually employed—in the case of iron, *must* be employed. In the latter case, the number of purposes for which thick deposits are required is very large. A somewhat thick deposit is required in electrotyping work; a still thicker one is often necessary in engineering work, as, for example, in "building up" work; and in such processes as the manufacture of printing rollers by electro-deposition, as, for example, in the Elmore process very thick deposits of copper are formed. In all cases where a thick deposit is required, the sulphate of copper solution should be used: except in a few cases it must be used, for the cyanide bath will not answer the purpose. Two types of solutions used for the electro-deposition of copper must, therefore, be considered, namely, the "alkaline" and the "acid." Of these, the latter is by far the more important, and will receive the larger share of attention here; but attention will be given to the alkaline bath, since this is, usually, badly neglected both in text-books and in workshop practice.

THE ALKALINE BATH

Chevreul's Salt. The solution which the author very strongly recommends is one made with a chemical compound known as "Chevreul's Salt." He is so convinced of the superiority of this salt over all others for the purpose of making an alkaline copper bath that the properties of the salt and a simple method of preparing it will be described. The compound is so called because it has been thought to have been first discovered by M. Chevreul, a distinguished French chemist. This idea is not accurate, for, though Chevreul investigated the properties and composition of the salt, and published a full description of his work in 1812,[5] he himself says that it was first made by MM. Fourcroy and

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[1] In Chapter I.

[2] *Electro-Deposition of Copper*, 1921. (Pitman.)

[3] The Germans distinguish between *Galvanostegie* and *Galvanoplastik*, the former relating to the production of thin deposits.

[4] Chap. I., p. 6.

[5] *Ann. Chim.*, 1812, vol. lxxxiii. p. 181.

Vauquelin. Its properties, and those of several other like compounds were studied, much later, by A. Etard.[1] G. Langbein claims to have introduced the salt into the copper-plating industry:[2] whether this claim is justified or not, its use in cyanide solution was advocated as long ago as 1906.[3]

1. *Preparation of the salt.* The method by which Chevreul's salt can be made, simply and by any one, from materials already in the plating-shop, is as follows: Dissolve 1 lb. of copper sulphate crystals in ½-gal. of hot water (60° to 70° C.) in an enamelled iron or stoneware vessel, and add the hot solution, gradually and stirring the while, to 1¾ lb. of sodium sulphite dissolved in hot water contained in a similar vessel. A dark red crystalline solid separates out, which should be allowed to settle. The supernatant liquid is then siphoned or poured off, and the copper salt washed two or three times with hot water. The salt need not be dried: it is sufficient to store it in a tightly-corked stoneware jar. The yield from each pound of copper sulphate will be about 8½ oz. of Chevreul's salt. The actual composition of the product obtained upon mixing copper sulphate solution with one of sodium sulphite depends upon the conditions obtaining and, especially, upon temperature.[4] Chevreul's salt will be formed under the conditions given, but if the temperature be much too high (or much too low) another sulphite or mixture of sulphites may be formed. The precipitate will then have a different colour; it may be pink or yellowish-red, and not dark red. If such a separation occurs, it is not a great matter from the plater's point of view, because, when the salt is dissolved in potassium cyanide solution (*vide infra*), the resulting solution will not be materially different from that obtained if Chevreul's salt alone had been employed. The conditions given for making the salts should, however, be adhered to as nearly as possible.

2. *Properties of the salt.* Chevreul's salt is a dark red crystalline substance. It will become oxidized to sulphate in moist air. It dissolves easily in a solution of cyanide of potassium, a slight evolution of sulphur dioxide gas (SO_2) occurring. In the trade it is called by various names—for instance, red copper, red copper sulphite, and sometimes, but wrongly, cuprous sulphite—as well as Chevreul's salt. Considered from the chemical point of view, it is a double sulphite of copper, and its chemical name is cuproso-cupric sulphite. Its chemical formula is $Cu_2SO_3, CuSO_3, 2H_2O$, and it contains 49·3 per cent. copper (metal).[5]

As has been done in the cases of the plating baths for depositing metals already dealt with, the cyanide of copper bath will be considered in relation to its composition, electrode reactions, and practical operation.

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[1] *Compt. rend.*, 1881, vol. xciii. p. 725; *ibid.*, 1882, vol. xciv. pp. 1422 and 1475; and *ibid.*, 1883, vol. xcv. pp. 89 and 137.

[2] *Electro-deposition of Metals*, 1909, p. 327.

[3] *Brass World*, 1906, vol. ii. p. 199.

[4] Just as does the composition of copper carbonate, *vide* S. U. Pickering, *Journ. Chem. Soc.*, 1909, vol. xcv. p. 1409, and H. D. Dunnicliff and S. Lal, *ibid.*, 1918, vols. cxiii. and cxiv. p. 718.

[5] The percentages of copper in other copper salts are: *copper carbonate*, varies, 49 to 51; *copper sulphate*, 25·45; copper Trisalt or Trisalyt, 21·2; *cuprous cyanide*, 71 (Brochet); *copper potassium cyanide*, 22·4 (Brochet)

(a) *Composition and Working Conditions*

1. *Composition.* The components should be in the proportions: 7 oz. of cyanide of potash (98 per cent. white, or 95 per cent. grey); 4½ oz. of Chevreul's salt; and 1 gal. of water.[1] Dissolve the cyanide in some water (hot, but not boiling), and then add to the solution the copper salt, little by little and stirring continuously, and, finally, add the remainder of the water. The brown insoluble solid which often separates is a complex cyanogen compound (called in the text-books "paracyanogen") of unknown composition. It is very light and, though bulky, does not amount to much in weight. It is useless, and should be filtered (or otherwise removed) from the solution before this is poured into the plating vat. The composition of this bath, though it cannot be described as simple, notwithstanding that the number of the original components is but two, is simpler than any other cyanide of copper bath. The Chevreul's salt supplies the metal: it also supplies sulphite, which is a useful substance in a cyanide bath. The potassium cyanide is necessary to bring the copper salts into solution; it also serves as a "conducting salt," and to bring the copper anodes into solution. Schlötter goes so far as to say that sulphite is essential (*wesentlich*) in the bath.[2] He describes one of its functions as follows: "In the course of the process" (of electrolysis) "a green layer forms on the anodes. This is probably cupro-cupri-cyanide, and it offers an enormous resistance to the passage of the current. The formation of this layer is more easily avoided by the addition of sulphites to the bath, and more easily dissolved when it is present." Brochet says[3] that the sulphite acts as a reducing agent of any copper present in the cupric state, itself being oxidized to sulphate. This may be true, and probably is so to some extent, but Schlötter's statement probably expresses the most important function of the sulphite: this is—in plain language—to keep the anodes clean, and it certainly does so in fact.[4]

2. *Working conditions.* The *specific gravity* will be about 9° Bé. at ordinary temperature: it should be kept between 9° and 11° Bé. *Current density* should be 3 to 4 amp./ft.^{2} *Temperature* of the solution should not be below 65° Fahr. (about 18° C.). If convenient, the bath should be worked at about 120° Fahr. (about 49° C.), since the higher temperature aids both the conductivity and the chemical action of solution of any salts separated on the anodes. *Agitation.* It is not usual to employ agitation in the case of the alkaline copper bath; but, as Brochet has said, it is much better to do so, if possible. Rod movement is sufficient.

(b) *Electrode Reactions*

Not much is known about the reactions that occur during the electrolysis of the alkaline copper bath, and such information as is available does not usually find its way into text-books on electro-deposition. Copper is deposited at the cathode and dissolved from the anodes, but in neither case is the current efficiency very good in workshop practice. It is not known whether the deposition of the copper is the result of primary or secondary action. A. Classen's view[1] is that the separation of metal is a secondary reaction—one, that is, of the type already seen to occur (according to Pfanhauser) in the case of the deposition of nickel from the double salts bath.[2] Classen says: "Thus we may assume that the solution contains some of the complex compound $K_2[Cu_2(CN)_4]$, which dissociates according to the scheme

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[1] Cf. baths given by G. Langbein, *op. cit.*, p. 327. W. Pfanhauser, *Galvanotechnik*, p. 378, and A. Brochet, *Galvanoplastie*, p. 203. F. C Mathers uses sodium cyanide in place of the potash salt, *op. cit.*, Note 6, p. 116 *post*.

[2] *Galvanostegie*, 1910, Teil 1, p. 137.

[3] *Op. cit.*, p. 199.

[4] Another possible function is mentioned by Steinach-Buchner in *Die galvanischen Metallniederschläge*, 1896, p. 106.

$$K_2[Cu_2(CN_4] \rightleftarrows 2K^+ + Cu_2(CN)_4^{--}.$$

During the electrolysis of the solution, the K^+ migrates to the cathode and is discharged there, while the $Cu_2(CN)_4^{--}$ migrates towards the anode. The $Cu_2(CN)_4$, however, cannot exist as such when the anion is discharged, but breaks down into cuprous cyanide, $Cu_2(CN)_2$, with evolution of cyanogen gas $(CN)_2$. Then the cuprous cyanide would be precipitated were it not for the fact that potassium cyanide is being formed by the reaction about to be described. At the cathode, the potassium that is set free reacts upon the undissociated complex salt and liberates copper, which is deposited upon the cathode; at the same time potassium cyanide is formed:

$$2K + K_2\,[Cu_2(CN)_4] = 2Cu + 4\ KCN.$$

This regenerated potassium cyanide dissolves the cuprous cyanide that has been formed at the anode." This explanation, similar to the old one of the separation of silver at the cathode from the silver potassium bath,[3] may or may not be correct. It has, at any rate, these advantages, namely, that it offers a rational and reasonably probable explanation of the phenomena, it has never been shown to be wrong scientifically, and it explains the facts of observation so as to allow the operator, cognisant of them, to control his bath. The alternative views are as complex as the salts in solution. They appear to be based largely on the work of Spitzer;[4] and, in short, seem to depend upon the idea that copper ions are supplied to the cathode as the result of the break-up of a complex anion, $Cu(CN)_2^-$, existing in the solution, thus:

$$Cu(CN)_2 \longrightarrow 2(CN)^- + Cu^+, \text{ and } Cu^+ \longrightarrow Cu + \oplus.$$

But those[5] who are prepared to allow of this idea for copper require something different in the exactly similar case of silver, in which case they say that the process of cathode discharge is not $Ag^+ \rightarrow Ag + \oplus$, discharge, that is to say, of a positively charged cation at the cathode—a process one can understand—but $Ag(CN)_2^- \rightarrow Ag + 2(CN)^- + \oplus$, which means that, at the cathode, a negatively charged complex splits up into negatively charged (CN) and neutral silver atoms. Unless the one expression given for silver is intended to represent the equivalent sum of the two given for copper, it is not easy to imagine the mechanism whereby silver becomes deposited. Those who hold this alternative are obliged to speak of reactions following one another at infinite speed in order that their explanation may hold: indeed, though the matter cannot be thrashed out here, the author is much inclined to think that theory has run wild in the case of cyanide baths.[1] As an instance of academic theoretical deduction, the following instance may be cited. After considerable argument about what are called cathode (or electrode) potentials, it is said by one author:

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[1] *Quantitative Analysis by Electrolysis* (trans. by Hall), 1913, pp. 47 and 48.

[2] Chapter IV., p. 33 (Reaction iv.).

[3] And due to W. Hittorf.

[4] *Zeit. f. Elektrochemie*, 1905, vol. xi. p. 345.

[5] *Vide* A. J. Allmand, *Principles of Applied Electrochemistry*, 1912, pp. 120 and 125.

"We see therefore that even at low current densities large quantities of hydrogen must be evolved simultaneously with the copper deposition. . . . The experience of the electro-plater corresponds fully with these results. Although the current density is low (0·3 amp./dcm.^{2}) yet the deposition of copper is accompanied by a violent gas evolution."[2] As a matter of fact, *violent* evolution of hydrogen is not a common phenomenon of the alkaline copper bath when properly worked in the shop, though considerable evolution may and does occur in cases *where a great excess of potassium cyanide is present.* Deposition of copper proceeds in the bath given above with very little evolution of hydrogen; and as regards the brass-plating solution, based on the double cyanides of copper and zinc, and, therefore, analogous to double cyanide baths of copper and of silver, Dr. Gore[3] says that if ammonium tartrate is added to the bath "evolution of hydrogen may usually be avoided, or should it, nevertheless, take place to a slight extent, *it may be entirely stopped* by the addition of some cupric ammonide." And Dr. Gore states that continuous deposition can proceed and thick coats of brass be obtained then: the practical man knows that thick solid deposits are only consistent with good efficiency, which, in turn, is consistent only with low hydrogen evolution. Spitzer's figures and those of Brunner[4] for silver solutions, and C. J. Wernlund's[5] for zinc cyanide baths, prove that, as a rule, reasonably, and, sometimes, quite good efficiency can be obtained with cyanide baths, when working under proper conditions; and F. C. Mathers[6] has shown that a bath he composed gave 100 per cent. efficiency at both anode and cathode. Such efficiencies are not consistent with copious or violent evolution of hydrogen, but are obtained in workshop practice from baths that do not contain an excess of cyanide of potassium, which undoubtedly increases the evolution of gas. It must be added that such high yields as Mathers obtained are not the rule in practical work: but the fact that they *can* be obtained, and at current densities, too, about twice as high as that usually employed with the alkaline copper bath, shows that any theory that leads to the remark that "large quantities of hydrogen *must* be evolved along with the deposition of copper" is faulty somewhere. The author, therefore, prefers, *as a working hypothesis*, and in the absence of any certainty, the former of the views mentioned; it is simple, and one that can be consistently applied to all cyanide baths. But it must, of course, be recognized that it is but an hypothesis, even though it enables one to exercise an intelligent control of the working of cyanide solutions.

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[1] For further information (in respect to silver potassium cyanide solutions) the following references may be consulted: H. Danneel, *Zeit. f. Elektrochem.*, 1903, vol. ix. p. 760, and F. Haber, *ibid.*, vol. x. p. 773. Allmand, *op. cit.*, summing up the authorities, says this view is "very probable," but that is as far as he goes.

[2] Allmand, *op. cit.*, p. 312.

[3] *Electrometallurgy*, p. 284.

[4] *Diss. Dres.*, 1907.

[5] *Trans. Am. Electrochem. Soc.*, 1921, vol. xl. p. 257.

[6] *Ibid.*, 1918, vol. xxxiv. p. 135.

(c) *Operation*

Table VI. indicates, in convenient form, some of the defects (or "troubles") met with when working with the cyanide of copper bath, the causes of them, and the remedies it is necessary to apply.

It has to be always remembered that cyanide baths are unstable, and changes in composition are the more rapid the higher the temperature at which the bath is worked. Moreover, the anode efficiency is not nearly so good as it is in the case of the acid bath. As a consequence, frequent additions of chemicals have to be made, including salts containing metal (copper). As regards the content of free cyanide, Mathers has found that very little is necessary to maintain the anodes in a clean condition. The best way to provide for the addition of metal salts is to make a strong solution of potassium cyanide, warm it up to about 120° Fahr. in an earthenware vessel, and add to it as much Chevreul's salt (in a moist condition) as it will dissolve. This should be done either in the open air or in a place where there is a good draught: it must not be done in a closed room. To aid solution of the salts, this, if dry, should be made into a paste with water; if this is not done, the dry particles of the salt will be surrounded by films of air which will prevent ready solution by the cyanide. When the saturation of the cyanide by the Chevreul's salt is completed, the solution should be allowed to cool somewhat, and then, after settlement of any solid and insoluble matter that may have separated, siphoned into a clean carboy, and kept as stock solution for addition, when needed, to the plating bath. Care should be taken that anodes are cleaned once a day at least. They should not be allowed to remain in the solution when this is not at work; for, if they are, they will almost certainly become "furred" or "choked" by a coat of some complex compound formed by the action of the components of the bath upon them. Another matter of importance is that if iron steam-pipes are used for heating purposes, and these are in the solution, as is often the case, these pipes must be insulated and not allowed to become in direct or indirect contact with the rods or the tank holding the solution.[1] The tank, too, ought to be insulated. More than once the author has found that the complaint of slow deposition was due to the fact that the sides of the tank were getting the deposit instead of the work. If the bath recommended above is employed, there is no reason why a

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[1] Cyanide solutions are nearly always contained in iron tanks. This has become common practice, but it is not good practice all the same. If tanks insulated on the inside were used, many of the troubles and much of the waste met with in the case of alkaline baths would be avoided.

wooden vat, lead-lined, and match-boarded on the inside, should not be used; but, in this case, care must be taken not to let the temperature rise above about 80° Fahr., and, further, care must be taken as to what arrangements for heating are employed.

TABLE VI

DEFECTS OF COPPER-PLATING (CYANIDE BATH)

Defect.	Cause.	Remedy.
1. Slow deposition	1. (*a*) Bath poor in metal. (*b*) Too much cyanide. This will be apparent from a too clean appearance of the anodes and from a too copious evolution of gas (hydrogen).	1. (*a*) Add some cyanide of potassium solution, saturated with Chevreul's salt. This should always be kept in stock in a carboy. (*b*) Add Chevreul's salt.
2. Low metal content.	2. This is due, especially, to inequality of anode and cathode efficiencies, which in turn is very often due to layers of non-conducting and insoluble slimes on the anodes.	2. Clean anodes. Add potassium cyanide or sodium sulphite. Remove anodes from the bath and clean them at the end of day's work.
3. Blue deposits on anodes.	3. Formation of cupro-cupri-cyanide.	3. Add sodium sulphite. Scour and clean anodes.
4. White deposits on anodes.	4. Formation of cuprous cyanide.	4. Add potassium cyanide. Scour and clean anodes.
5. Solution a blue colour.	5. Insufficiency of cyanide.	5. Add potassium cyanide.
6. Blisters on deposit.	6. (*a*) Low metal content. (*b*) Too much cyanide. (*c*) Too high current density.	6. Remedies for all those causes are obvious.

THE ACID BATH

(*a*) *Composition*

As before stated, the two components of the acid bath are copper sulphate (the "blue vitriol" of commerce) and sulphuric acid (oil of

vitriol). Proportions that will serve many purposes are: 2 lb. sulphate (free of arsenic), 6 fluid oz. of acid (1·820 sp. gr.), and 1 gal. of water. The sulphate may be good commercial salt, and the acid should be pure white vitriol; the latter must not contain such impurities as iron, lead, and arsenic, which are often to be found in impure and cheap acid. The composition given above is that of a, so to say, standard bath; but it may be necessary, in specific cases, to add more of either or both components. For instance, S. Cowper Coles used as much as 10 per cent. of acid in his bath for depositing copper on rotating cylinders.[1]

(b) *Working Conditions*

The *specific gravity* of a bath of the composition given will be 14° to 16° Bé. *Current density* may be from 10 to 15 amp./ft.^{2} in "still vat" work, and 15 to 20 amp./ft.^{2} with agitation. E.M.F. varies with the rod distances, number of anodes, and temperature, among other things. At 9-in. rod distance, 2 to 3 volts is usual with a full load of work. *Anodes*: good commercial metal (guaranteed free of arsenic and sulphur) should be used. Electrolytic copper, though purer, often causes trouble through not having been properly heat-treated. *Agitation*: rod movement at least should be used. Another good method of agitating the solution is to employ a suction and force pump driven by a small motor. Agitation by blowing in air—a common practice—is bad.

(c) *Operation*

The acid bath is commonly considered quite simple to work. It is easy enough to obtain copper deposits from it, but to obtain deposits that are really such as are, or ought to be, sought is not by any means the simple matter it may seem. It is, in the case of this bath, very necessary that the operator should know what physical and mechanical properties he requires the deposit to possess, and suit the conditions of deposition to the formation of metal having these properties. This requires skill and knowledge and much more care than is usually given. It has been stated by C. W. Denny,[2] regarding a particular case that: "the process, which is comparatively simple, requires a skilled depositor to take care of the innumerable details which demand study and attention if successful results are to be obtained." This is true in general, and not in this or that particular case merely. The operator must keep a careful eye on both the macroscopic aspect of the deposit and the wear of the anodes. He must keep the current density and the composition of his bath approximately constant; and *he must keep the bath clean* and free from floating matter. It is always good practice to keep plating baths clean: it is a *sine qua non* where a thick deposit is required. One and a principal source of floating particles is the material of the anodes, whether this is electrolytic copper or ordinary commercial metal. When the former is used, it is not infrequent to see the anodes covered with a loose, powdery material, which becomes detached and floats in and on the surface of the solution. This is a copper dust, formed through the disintegration of the anodes. These consist of very small crystals,[1] which are attacked along their junctions during the electrolysis of the solution, and become separated from one another. Proper heat-treatment would have prevented this; but if this has not been given to the anodes, such a dust as has been described will be formed: On the other hand, anodes of ordinary copper contain impurities which, as the anodes dissolve under the action of the current, are left as and form a sludge on their surfaces, and this sludge is always liable to become detached. The way, and the only way, to avoid the troubles caused by floating particles derived from the anodes is to interpose a filter or strainer between anodes and cathodes. This can be done with very little trouble. Thus, either the anodes can be enclosed in linen or fine canvas bags that more or less fit them, or a screen can be formed by stretching a piece of linen, or the like, over a wooden frame, and fixing this simple form of filter in front of the anodes. Very little ingenuity is required to devise a suitable and simple means of preventing anode detritus from reaching the work. Any trouble taken will be well and surely repaid. The author is not advocating anything elaborate or unpractical: he is suggesting to others that they should do what he himself has, many times, done in workshop practice. Floating particles are due, too, to allowing vats to remain uncovered when not at work, or allowing assistants to "sweep up" while the vats are uncovered and without previously watering the floor. And, thirdly, they may be caused by stirring up the sludge at the bottom of the vats either during agitation or when adding salts or acid. The depositor must take care to remove at once any articles (especially iron ones) that drop into the solution; this precaution is of special importance in the case of the acid copper bath. A number of the defects met with when working the bath, and their causes and remedies, are pointed out in Table VII. This form of presentation is more convenient and simpler than detailed description.

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[1] *Trans. Far. Soc.*, 1905, vol. i. p. 223. The solution used by Coles was: Copper sulphate, 32 oz.; sulphate acid, 12·6 oz.; water, 1 gal. (vide *Jour. I.E.E.*, 1900, vol. xxix. p. 276).

[2] *Electro-deposition of Copper*, p. 56 (Pitman).

(*d*) *Electrode Reactions*

The acid copper bath, though apparently so simple in composition, has been the subject of much scientific investigation. The result of it all is that, even to-day, there is some difference of opinion as to what exactly the electrode reactions are. A full discussion of the position would be out of place here, nor is it necessary. What is especially needful is that a competent operator, or one who has to supervise the process of copper deposition, should be able so to visualize the mechanisms of the reactions at anode and cathode as to be able, with considerable knowledge, to control his baths with confidence. Exact and complete information is not a necessity for practical purposes, even if it could be attained. Advantage will be taken of the opportunity here offered to consider electrode

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[1] Cf. Steinach and Buchner, *op. cit.*, p. 128.

TABLE VII

Defects of Copper-Plating (Acid Bath)

Defect.	Cause.	Remedy.
1. *Rough* deposit, surface gritty or covered with *outgrowth, lumps, or warts*: sometimes scored.	1. *Floating Particles.* (*Vide* also 5 *infra.*)	1. *Filter* solution and keep it clean.
2. *Sandy* deposit, surface fairly smooth, of coarse grain, but not obviously crystalline.	2. (*a*) *Too little free acid.* (*b*) *Need for agitation.* (*c*) *Too little metal* (copper): bath too dilute.	2. Remedies are obvious.
3. *Crystalline aspect* .	3. If the composition of the bath is correct, then a crystalline (especially a coarsely crystalline) aspect shows that agitation or increased agitation is necessary.	3. Remedy—obvious.
4. *Dark or red colour*—especially at edges and corners. The colour should be salmon pink and uniform.	4. *Too much current.*	4. *Lower current*, or *agitate* if movement has not been used.
5. *Dark colour* over general surface, together with a rough surface.	5. *Too little free acid.* The acid prevents the formation of cuprous oxide at the cathode cuprous oxide has a dark colour, and, becoming entangled in the deposit, makes this rough.	5. *Add acid*—carefully.
6. *Black or brown streaks.*	6. *Impurities* in the bath, *e.g.*, and especially *Arsenic.*	6. *Suspect anodes* and *acid* used. The only remedy is "working out" (*vide* Table III., col. 3, of Chap. VI.). For a method of detecting arsenic, see any text-book on chemical analysis. The test called "Marsh's" is a good one.

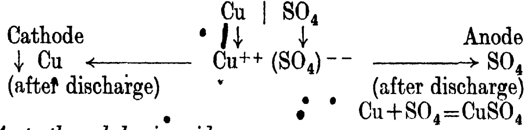
TABLE VII—*continued*

Defect.	Cause.	Remedy.
7. *Bright* deposit . .	7. *Impurities*—probably organic matter, *e.g.* glue or resin from the wood of the vat: sometimes arsenic will cause brightness.	7. *Working out.*
8. *Pitted* deposit . .	8. (*a*) *Too much acid*—causing gas evolution. *N.B.*—In this case the deposit is formed slowly, but what there is has a good colour. (*b*) *Too much current.* *N.B.*—In this case the deposit will be dark, especially at corners and ridges—*i.e.* "burnt." (*c*) *Need for agitation.* Long-continued deposition in a "still vat" causes the cathode layer of liquid to become weak in metal, and as a result hydrogen is liberated.	8. The remedies to be applied are obvious.
9. *Brittle* deposit . .	9. This is usually due to the kind of internal structure of the deposit. A coarse-grained deposit is, in the case of copper, usually brittle. So, too, is a sandy deposit (*vide* also 2 and 3 *supra*).	9. The conditions of deposition must be amended and those adopted which will give a deposit of fine grain and malleable metal. Agitation is often helpful.
10. *Hydrogen evolution*—resulting in pitting and dark deposit.	10. *Too much current and/or acid.* The deposit is dark owing to inclusion of cuprous oxide (Cu_2O). Cf. F. Förster and Seidel, *Zeit. Anorg. Chem.*, 1897, vol. xiv. p. 106.	

reactions from the point of view of what is called the Electron Theory. What is said below in that regard is applicable not only to the acid copper bath, but to the electrode reactions that occur in solutions of salts of other metals. Unless the reactions are considered from that point of view, no sufficiently satisfying mental picture of their mechanisms can be formed or one that accords with the discoveries of modern science.

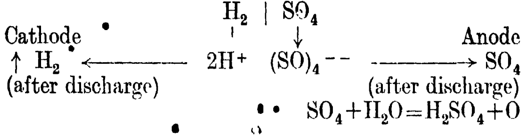
1. The general way of setting out the electrode reactions in the case of the acid copper bath is represented graphically in some such way as the following in the better text-books on electro-plating:[1]

(i) *As to copper sulphate*—



$$\begin{array}{lcr} & Cu \mid SO_4 & \\ \text{Cathode} & \downarrow \quad \downarrow & \text{Anode} \\ \downarrow Cu \longleftarrow & Cu^{++}\ (SO_4)^{--} & \longrightarrow SO_4 \\ \text{(after discharge)} & & \text{(after discharge)} \\ & & Cu+SO_4=CuSO_4 \end{array}$$

(ii) *As to the sulphuric acid*—



$$\begin{array}{lcr} & H_2 \mid SO_4 & \\ \text{Cathode} & \mid \quad \downarrow & \text{Anode} \\ \uparrow H_2 \longleftarrow & 2H^+\ (SO)_4^{--} & \longrightarrow SO_4 \\ \text{(after discharge)} & & \text{(after discharge)} \\ & & SO_4+H_2O=H_2SO_4+O \end{array}$$

The interpretation is that: (*a*) molecules of copper sulphate and sulphuric acid split up, on solution in water, into copper and hydrogen cations and sulphanions, $(SO_4)^{--}$. (*b*) The former, being positively charged, move to the negative electrode and become neutralized there, while the sulphanions, being negatively charged, move to the anode and are neutralized there. (*c*) After becoming neutralized, the atoms of hydrogen and the complex radicles (SO_4) react *chemically*. Hydrogen atom unites with hydrogen atom to form molecules (H_2), which, under certain conditions, escape as gas. The sulphate radicle may cause the copper anode to dissolve and, thus, copper sulphate to be formed; or, as shown in (ii), it may react with water, giving rise to sulphuric acid and oxygen gas. Field says[2]: "The H ions move to the cathode and *there they turn out copper*—

$$2H+CuSO_4=H_2SO_4+Cu."$$

He may be right in part; certainly no hydrogen gas *appears* at the cathode, when the acid copper bath is worked under normal conditions; and W. Pfanhauser thinks that hydrogen may play some such part.[3]

2. The above schemes undoubtedly represent a good deal of the truth concerning the electrode reactions in the acid copper bath. Even, the representation as to what becomes of the hydrogen after the hydrions are discharged at the cathode may be true at times, *e.g.*, if too much current is employed. But research has shown that they must be taken to represent *end* or *general* results only; they do not represent all the truth. They will suffice, *as a minimum*, the needs of a depositor; but, in these days, more should be known of the mechanism of electrode reactions, and especially those of the acid copper bath—always provided

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[1] Cf. S. Field, *The Principles of Electro-deposition*, 1911, p. 168. (Longmans.) This book is intended for use in the laboratory.

[2] *Op. cit., loc. cit.* Field means—The hydrogen *atom* resulting from discharge of the hydrogen *ion* turns out the copper. The hydrogen *ion* does not do so, of course.

[3] *Die elektrolytischen Metallniederschläge*, p. 675.

idle speculation is not indulged in, as has been done in the case of the cyanide bath. This requires a statement of the happenings at anode and cathode during electrolysis that is more accordant with modern views. E. Fournier d'Albe[1] has stated them thus for the case of hydrochloric acid—a very simple case :

" The H atoms[2] arrive at the negative plate, which contains a vast number of electrons[3] ready to pass out of the metal into the solution on the slightest provocation. Such provocation is supplied by the H ions, which, having lost an electron each, are positively charged, and attract electrons out of the metal. When this takes place the positive atom of hydrogen becomes a neutral atom. It immediately disengages itself from the embrace of the water molecules which have clung to it during its charged state, attracted by some as yet mysterious force, and becomes an ordinary gas. As it accumulates, its pressure becomes such that the water can no longer hold it in solution, and it escapes from the water in the shape of bubbles."

At the anode the converse process happens meanwhile. The chlorine ion, having an electron to spare, lets it pass into the positively charged plate, and the chlorine atom becomes ordinary, neutral chlorine gas. In the case of a solution of copper sulphate, the copper is deficient (most of it) of *two* electrons, and the sulphate ion has *two* to spare. Hence, *two* electrons must pass from the cathode to the copper ion in order to make it an electrically neutral atom of copper ; and, similarly, at the anode, each single sulphate ion parts with *two* electrons to the anode plate.

Using the modern notation, the case of copper can be represented thus :

$$\left.\begin{array}{l}\text{At the cathode } Cu^{++} + 2\ominus \longrightarrow Cu \\ \text{At the anode } (SO_4)^{--} - 2\ominus \longrightarrow (SO)_4\end{array}\right\}^{4} \quad . \quad . \ (1)$$

The important thing for the depositor in the workshop is that he should always be picturing in his mind these electrode reactions or happenings. The cathode surface should be pictured as the locus of a vast number of electrons—units, that is, or, as one may say, atoms, of negative electricity ; and the process of the arrival of the copper ions at the cathode, the dropping of the water molecules in some way attracted to them, and the actual process of the taking up of electrons by the ions should all be mentally conceived. The way these reactions are represented on paper is of secondary importance ; it is just a convenient chemical shorthand. It will be noted that consideration of the electrode reactions from the point of view of the electron theory gives more meaning to such phrases as "discharge at the cathode" (or anode); the mechanism of discharge becomes clearer and more real to the mind.

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[1] *The Electron Theory*, 1906, p. 110. (Longmans.)

[2] He means " *ions*," not " *atoms*."

[3] " *The atom of negative electricity*, which, like the atoms of any one element, are all precisely of the same kind, and, so far as is known, are not divisible into smaller units, is termed the *electron* " (F. Soddy, *Matter and Energy*, p. 151 (Williams & Norgate)).

[4] Cu^{++} signifies a copper atom with two positive charges—one, that is, that has lost two electrons. It is the copper ion. The symbol $\ominus$ represents the atom of negative electricity—the electron. $(SO_4)^{--}$ signifies the sulphanion—the sulphate complex (SO_4) carrying two electrons to spare. It is thus charged with two atoms of negative electricity. The sulphanion is sometimes written thus : $(SO_4\ominus\ominus)$. Chapter VI. of Prof. Soddy's little book will well repay careful study in connection with this matter.

3. Other reactions are known to occur at both anode and cathode besides the simple ones just described, and they have to be taken into account. There may also take place at the cathode a reaction represented thus:

$$Cu^{++} + \ominus \longrightarrow Cu^{+} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

which reads—a copper atom minus two electrons (which is equivalent, electrically, to carrying two units of positive charge) takes up one electron at the cathode, and becomes a copper atom minus *one* electron. The former is called a *cupric* ion; the latter a *cuprous* ion. These cuprous may, in their turn, be discharged, thus:

$$Cu^{+} + \ominus \longrightarrow Cu \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3),$$

which reads—a copper ion minus one electron (which is equivalent, electrically, to carrying unit positive charge), takes up an electron at the cathode, and becomes an electrically neutral atom of copper.

The ways in which these three cathodic reactions are represented in many text-books are somewhat different from those given.[1] The usual way of presenting them is:

1. $Cu^{\cdot\cdot} \longrightarrow Cu + 2\ominus$ — *i.e.*, cupric ions to metallic copper. It corresponds to 1.
2. $Cu^{\cdot\cdot} \longrightarrow Cu + \ominus$ — *i.e.*, cupric to cuprous ions. It corresponds to 2.
3. $Cu^{\cdot} \longrightarrow Cu + \ominus$ — *i.e.*, cuprous ions to metallic copper. It corresponds to 3.

It is suggested that these forms of presentation[2] are not so easy to read, and it can be argued that they are capable of misleading. The practical man needs some shorthand way of representing what he can see in his mind's eye. This need is not supplied by this last set of presentations: it is by the former set. The author, therefore, for that reason especially, but for many others also, prefers to follow Lehfeldt and others.[3]

4. When the sulphate ions become neutral sulphate radicles at the anode, they attack the material (copper) of it, and metal passes into solution. The shorthand method of presenting the happenings at the anode shows how this solution occurs. Thus:

$$\begin{array}{l} Cu - 2\ominus \longrightarrow Cu^{++} \\ Cu - \ominus \longrightarrow Cu^{+} \\ Cu^{+} - \ominus \longrightarrow Cu^{++} \end{array}$$

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[1] Cf. R. Abegg's *Handb. d. Anorg. Chem.*, 1908, vol. ii., Part 1, p. 476 (Hirzel, Leipzig). And see T. R. Brigg's modification of R. Luther's theory, *Trans. Am. Electrochem. Soc.*, 1921, vol. xl. p. 231.

[2] Reading from right to left, one sees what happens at the anode—the same happenings as are put in a different way in subsection (4).

[3] *Electro-Chemistry*, Part 1, pp. 12 et seq. (Longmans.) And cf. M. le Blanc, *Lehrb. d. Elektrochemie*, 1911, p. 13. (Leiner, Leipzig.)

These may be read :

An atom of copper is deprived of *two* electrons, and becomes a *cupric* ion—doubly and positively charged.

An atom of copper is deprived of *one* electron, and becomes a *cuprous* ion with a single positive charge.

A *cuprous* ion is deprived of another electron, and becomes a *cupric* ion.

When do these things happen ? And how does the discharge of the sulphanions bring them about ? These are questions to which answers have to be given : one cannot slur over them or (ostrich-like) ignore them. It has been well said that when an author writes with a misty profundity, it is a safe rule to assume that he is talking nonsense.[1] The truth is that neither of the two questions just put can be given a rigidly exact answer—scientific knowledge does not suffice. But a mental picture (*eine Vorstellung*, as the Germans say) of what may very likely happen can be formed, and it is one that does not seem overdrawn. The sulphate radicles, one can imagine, attack the atoms of copper of the electrode, attach themselves to them, and drag them into the solution, the process being assisted by a force,[2] already acting on the copper atoms, that tries to force them into the solution. Molecules of copper sulphate of this origin are thus existent, at any rate momentarily. Some of them are ionized—that is, split up into ions—no one knows how. In most cases the copper atoms are deprived of two electrons (formation of *cupric* ions) ; in a few, of only one (formation of *cuprous* ions) : in certain circumstances an atom already deprived of one electron will be deprived of still another (formation of cupric ions from cuprous). The answers will be, then (on this view), that the sulphate radicles (the discharged sulphate ions) bring the copper atoms into a medium in which the two are then, many of them, separated again—perhaps by the actions of the water molecules.[3] Only now, after separation, the two parts of each molecule are charged, because, on separation, the copper lost two electrons, and the sulphate radicle gained two. This view of the mechanism of the anode reactions suffices to enable the operator to understand better the end result that occurs at the anode, namely, solution of copper. Their final representation has already been given.

The foregoing discussion of the electrode reactions that occur during electrolysis of the acid copper bath is not of academic interest merely. The author has found knowledge of the facts enclosed in it of great use in the workshop, when face to face with difficulties that occur in daily practice. For the sake of clearness, and by way of summary, it may with advantage, perhaps, be again pointed out—(*a*) That a knowledge of the reactions as set out in sub-section (1) above is sufficient, *as a bare minimum*, for the practical man, or, better said, for workshop practice ; (*b*) that when these are considered from the point of view of the electron theory the actual mechanisms at the electrodes become more vividly portrayed to the mind ; and (*c*) that the presence of cuprous ions in the solution has to be kept in mind, and taken into account.

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[1] A. N. Whitehead, *Introduction to Mathematics*. (Williams & Norgate.)

[2] The so-called *electrolytic solution pressure*.

[3] *Vide* G. D. Hinrichs' View, Chapter II., p. 17.

It is very probable that what has been said does not exhaust, even in outline, the subject of electrode reactions in the acid copper bath. It is certain that there exist in this bath, as usually employed, complex anions of the type $(HSO_4)^-$, as well as the sulphanions, $(SO_4)^{--}$; and A. Hollard's work on the conductivity of mixed electrolytes shows that other complex ions exist in the bath.[1] But it is unnecessary, except where one intends to undertake pure research work, to be concerned with the minor or exceptional reactions: the main ones are those of importance to the practical man.

STRUCTURE

The consideration of the structure of electro-deposited copper is dealt with in Chapter XI. in connection with an outline description concerning the structure of deposited metal in general. It may, however, be noted here that structure is of very great importance, for it has been definitely established by the experimental work of Kiliani,[2] von Hubl,[3] Förster, and Seidel[4] and others, that the properties of the deposited copper depend upon its structure, and these, in turn, upon the conditions of depositions.

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[1] *La Théorie des Ions*, pp. 200 et seq. (Gauthier-Villars, Paris). See also R. Abegg, *op. cit.*, p. 545. The article on copper, contained in Abegg's handbook and written by Prof. F. G. Donnan, is a masterpiece of scientific writing. It contains, too, a full list of references to original researches carried out on the acid copper bath.

[2] *Berg und Huttenmannische Zeitung*, 1885, p. 249.

[3] *Mitt. des k. u. k. militargeog. Inst.*, 1886, vol. vi. p. 51.

[4] *Zeit. f. Elektrochem.*, 1899, vol. v. p. 508.

CHAPTER XI

THE STRUCTURE OF ELECTRO-DEPOSITED METAL

IN the previous chapter[1] advantage was taken of a favourable opportunity to introduce the modern view of electrolysis—that is, the view that makes use of the electron theory and the present-day conception of the atomic nature of electricity, foreshadowed by Helmholtz in his Faraday lecture before the Chemical Society in London.[2] The purpose of the present chapter is to consider the structure of electro-deposited metals. In doing so, greater prominence will be given to the structure of copper, since the structure of this metal has been more thoroughly investigated than that of other deposited metals.

CRYSTALLIZATION

It is now a matter of almost general agreement that electro-deposited metal is, with few, if any, exceptions, crystalline material.[3] So abundant is the evidence for this view, and so general is it, that it would not be profitable to discuss the matter here. Deposited metal being, then, crystalline, the laws of crystallization that govern the formation of crystals of other substances, such as salts, igneous rocks, and metals as formed in ordinary metallurgical processes, may be expected to hold in the case of metal formed during electrolysis. An attempt has been made elsewhere to work out the validity of that idea, and, in illustration, the structures to be found in deposited iron were considered.[4] Broadly, it may be said that the two factors which determine the structure of a crystalline mass are (1) the formation of nuclei, and (2) crystal growth. A crystal must have an origin in space. This is usually referred to—somewhat indefinitely—as a nucleus. The nucleus, or, better, the embryo, is really the initial and unit aggregate of atoms arranged spatially in an ordered manner by the so-called "forces of crystallization." It forms a centre of growth. The greater the number of embryos formed in unit time in unit volume, the smaller the grain-size of the crystalline mass will be when formed. If the number of embryos formed is small, the grain-size of the mass will be large. The factor, super-saturation, governs both formation of nuclei and also crystal growth; unless the medium in which the crystal originates or grows is super-saturated with the substance of which the crystal consists, crystallization cannot occur.

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[1] This chapter may be read at an earlier stage if convenient.

[2] *Jour. Chem. Soc.*, 1881, vol. xxxix. p. 277.

[3] Cf. F. Förster, *Elektrochem. wäss, Lösungen*, 1922, p. 384 ff.

[4] *The Electro-deposition of Iron*, published by H.M. Stationery Office.

A word of explanation is necessary as regards the expression "super-saturation." One substance, *A*, is said to be super-saturated by another, *B*, when under the conditions of temperature and pressure prevailing, it contains more of *B* per unit volume than it can retain in the dissolved state under these conditions. The difference between the amount it can retain under given conditions and that actually contained in it will be deposited upon slight provocation, such as shaking, sowing with a small crystal of *B*, and so on. The solution is super-saturated to that extent. As a general proposition it may be said, that the greater the degree of super-saturation, the quicker the deposition of the excess and the smaller the crystal grains will be.

Influence of the Rate of Deposition

(i) *Slow Deposition*

If the foregoing statements of the laws governing the crystallization of substances in general be borne in mind, then present-day knowledge of the facts of metal deposition enables one to understand the structures that may be seen in deposited metal, when this is examined with a microscope. For instance, other workers,[1] as well as the author, have observed that coarse-grained structure is associated with slow and undisturbed deposition; this has been found to be so in the cases of iron,[2] zinc, copper, and cadmium. Slow deposition means that comparatively few atoms of metal are *available* for the formation of crystals. Hence, the super-saturation of the layer of solution next the cathode surface will be slight. In the case of salts, such a condition of things leads to the formation of large crystals, and, thus, there is found to exist an association of slight super-saturation with coarse structure in the cases of both crystalline substances in general and electro-deposited metal. It seems an inevitable conclusion that coarse (that is, large-grained) structure is caused by, or is the result of, slow deposition. If one forms a mental conception of the habitants of unit volume of the solution adjacent to the cathode surface, conviction becomes still greater. Such a unit volume is the locality of moving molecules of each of the constituents in the solution, of ions of the various components—including, of course, metal ions, and of discharged ions—of atoms, that is to say. As regards the free, discharged atoms of metal, these, except in so far as they interact with other substances, are free to unite and form crystal grains of the metal. In order that the atoms may form a crystalline embryo, enough of them must come sufficiently close together; and the fewer there are in unit volume (that is to say, the less the super-saturation), the less likely this is to occur. What will be more likely is that the individual available atoms will come under the influence of one or other of the crystal grains forming the mass of the deposited metal, and, thus, that these grains will "grow," and this grain-growth leads, of course, to coarse structure. It is interesting to consider when deposition will be slow or, in other words, when the availability of atoms for formation of the deposit will be small. It will be convenient to do so in separate divisions.

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[1] Cf. M. von Schwarz, *Inter. Zeit. f. Metallographie*, 1915, vol. vii. p. 124. Also *vide Jour. Inst. Metals*, 1920, vol. xxiii. p. 525.

[2] *Vide* "Idiomorphic and Hyp-idiomorphic Structures in Electro-deposited Metal," *Trans. Am. Electrochem. Soc.*, 1922, vol. xli. p. 317. Sieverts and Wippelmann (*op. cit.*, Note 3, p. 130) found that largeness of grain was associated with low current density even though some measure of agitation of the electrolyte was employed.

Deposition will be slow in the following cases:

(*a*) *When the current density is small,* for, in this case, the total number of ions liberated at the cathode per unit time is small. If all the resulting metal atoms are available, the number free to form metal is still small; but, in many cases, the whole of them will not be available. Chemical interaction between the liberated atoms and the components of the medium surrounding them may occur, as happens to a very great extent in the case of the alkali[1] and alkaline earth[2] metals, and also in the cases of magnesium, aluminium, and others. In these cases the number of free and available metal atoms will be still smaller, and may be very small indeed.

(*b*) *Deposition may be slow even though the current density be great, or, at any rate, considerable.* This is a very interesting case to consider, because some confusion has arisen in the past in interpreting the structures obtained when higher current densities are employed. In regard to the observed results it can, fortunately, be said that there is considerable measure of agreement between those obtained by different investigators, working at different places and times and upon different metals. Sieverts and Wippelmann published their results in 1915,[3] and worked on *copper.* They found that, at low current density, the crystallites were large; but, as the current density was raised, the following alternations of grain-size occurred. Large grains were succeeded by small grains until a certain limit of current density was reached, the limit varying, in each case, with the other prevailing conditions of deposition. After the limit, in any case, was attained, the grains became larger again, while, at the highest current density they used, Sieverts and Wippelmann found the structure to be so irregular and broken that it could not be interpreted. In the author's recent (1922) publication on deposited *iron*[4] a similar alternation is mentioned as occurring in deposits of that metal formed at different current densities, but under otherwise the same conditions. It may, therefore, be said that it has been found that increasing current density gives, first, coarser structures and then finer. If, now, coarse structure is associated with slow deposition (as has been suggested above), then, as current density is increased up to a limit, so deposition should become slower, since structure becomes coarser. At first appearance this seems unlikely; but consideration of what happens in the cathode layer of solution alters the *prima facie* impression. Suppose one has two cells side by side in which copper, say, is being deposited, and suppose all the conditions are the same in the two, except that in one the current density is *considerably* higher than in the other, yet not very great. Then the experimental results cited above show that the deposit in the former cell will consist of larger grains than those composing the deposit formed in the latter. If the happenings in the cathode layers of solution be mentally visualized, one sees this layer becoming more quickly exhausted of its metal content in the cell in which he current density is higher.[1] Deposition of copper will, therefore, become slower, since, as the concentration becomes lower, the amount of copper ions available for discharge and, consequently, the number of atoms of copper available for metal formation become, both of them, less. And this is so, although the current density remains constant. So long as the current density does remain at a constant value, the liberation of ions must, it is true, remain of equivalent constant value too, as we know from Faraday's law. But the ions discharged will not be, all of them, copper ions. The ions freed will be copper ions, plus a number (x, say) of ions other than those of copper—hydrogen ions, for instance; and x will increase as the concentration and, consequently, the discharge of copper ions diminishes. In the cell in which the current density is ess, the cathode layer of solution will, in this case too, become gradually exhausted of its metal, but the exhaustion will, *ceteris paribus*, be much more gradual and, thus, although the deposit will be coarse-grained, yet t will be less so than that formed in the other cell. There are several mplicit assumptions underlying the foregoing argument; these will be pointed out later. The object for the moment is to show how it is that high current density *may* result in coarse-grained structure—structure of larger grain than those of deposits formed at lower densities. This may now be stated, in few words, as being the result of the slower deposition of *copper* at higher current densities, consequent upon the quicker exhaustion of the copper in the cathode layers of solution.

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[1] Sodium and potassium. [2] Calcium, barium, and strontium.

[3] *Zeit. f. Anorg. Chem.*, 1915, vol. xci. p. 1, and *ibid.*, vol. xciii. p. 287.

[4] *Op. cit., vide* p. 128.

(*c*) It follows from what has been said above that *slow deposition occurs when metal concentration is low.* Workshop experience confirms this. When, using the normal current density, a plater finds that, as he says, " the bath works slow," the first thing he does (and rightly does) is to add more metal salts to it.

(*d*) *Deposition of metal will, also, be slower at lower temperatures than at higher.* This results from the fact that the electrical conductivities of liquids (electrolytes) increase as the temperature rises, in contradistinction to the cases of most metals, where conductivity decreases with rising temperature. The electrical result of decreased conductivity is that, at constant potential difference, the quantity of electricity flowing through the solution diminishes. Now, the quantity of electricity reaching the cathode per unit time depends upon the number of ions that get there, their charges, and their mobility. Since the charges on the ions will not be affected at all and the ionic velocities very little as the temperature falls, the number of ions reaching the cathode must decrease and, hence, the availability of metal atoms will diminish. Consequently, deposition will be slower. Here, too, practical experience in the plating shop confirms laboratory results. It is not uncommon to find that, after a holiday period during the cold season of the year, plating baths work badly. The deposits are formed very slowly on the goods, and if an attempt is made to increase the rate of working by raising the current, evolution of gas occurs and the deposit is spoiled. As a consequence of deposition becoming slower as temperature falls, one might expect that, as the temperature rises, deposition will become quicker, and, as a result, the structure of the deposit more fine-grained. And this certainly is the result *within limits*. But rise of temperature may, when it has become sufficiently great, introduce another factor—movement—which will partly or, in some cases, entirely, mask the effect of temperature in and by itself. The deposit will, in this case, appear more fine-grained than it would do if the factor of deposition—temperature—were alone in play. Again, temperature increases the conductivity of the solution *as a whole* and not merely its conductivity in regard to its copper sulphate content. This, too, may cause the effect of temperature alone to be masked; the structure of the deposit may become coarser instead of finer.[1] These matters will be considered later. It is sufficient to note here that the result of fall of temperature should be slow deposition, and that this should result in coarser structure. M. von Schwarz has shown that it does so.[2]

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[1] Cf. K. Arndt and O. Clemens, *Chem. Ztg.*, 1922, vol. xlvi, p. 925.

(*e*) *Excess of free acid will cause slow deposition.* In some cases, as, for instance, in that of the nickel bath, excess of acid will prevent deposition of metal entirely. An instance has been given in Chapter VI.[3] Another sometimes occurs during the estimation of copper by electro-analysis. If too much nitric acid is used, the copper deposit will, at some time before deposition is complete, be found to redissolve, notwithstanding the continuous passage of the current. To prevent this re-solution, urea is often added to the electrolyte as prepared for analysis[4]; but the real preventative is to take care not to employ too much acid to begin with. It cannot be said that the association of slow deposition with coarse structure has been proved, where slow deposition is due to the presence of excess of acid; indeed, free acid has been shown to cause *diminution* of grain-size.[5] Further reference will be made to this matter later on.

(ii) *Quick Deposition*

Since one observes that slow deposition is associated with coarse structure, it is natural to suppose that the converse will be true, and that the association of quick deposition with fine-grained structure will obtain. And, as a fact, it often does. Deposition will be rapid in the following cases: (*a*) When the current density is high and, at the same time, the concentration of metal in the cathode layer is maintained continuously great. The condition as to continuous metal concentration should be noted. (*b*) Deposition *may* be rapid when the concentration in metal is great, provided the current density is high enough. There may not appear, *prima facie*, to be much difference between statements (*a*) and (*b*). The difference is (and it is of great importance), that (*a*) tells us when high current density will result in rapid deposition, and (*b*) when great metal concentration will do so. (*c*) Deposition will be rapid also when the temperature is high, provided it is higher than a maximum which varies from case to case. The matter will be considered more fully under the paragraphs dealing with the factors of deposition.

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[1] As the author has found it to do in the case of iron deposited at temperatures of the order 200° C.

[2] *Internat. Zeit. f. Metallographie*, 1915, vol. vii. p. 124.

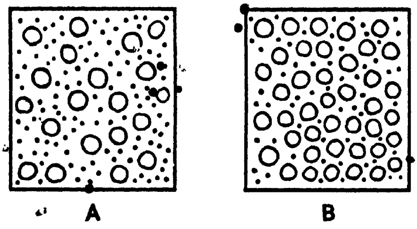
[3] Chapter VI., Table II., 3rd column, sub-heading "To detect copper."

[4] V. H. Veley, *Phil. Trans.*, 1891, vol. clxxxii. p. 279; E. Gilchrist and A. C. Cumming, *Trans. Far. Soc.*, 1913, vol. ix. p. 186.

[5] *E.g.*, by the author, vide *Trans. Far. Soc.*, 1922, vol. xvii. p. 442.

A very important matter for remark in connection with quick deposition is that the effect actually produced by each of the conditions of deposition which, if it acted alone, would effect rapid deposition and, consequently, small-grained structure, is affected much more powerfully by the remaining factors of deposition than is the effect of a condition causing slow deposition. It has been seen that high current density may lead to coarse structures instead of fine. It will do so in "still vat" work—in work, that is to say, done in the absence of mechanical agitation of the solution or movement of the electrodes and, in particular, of the cathode. If current density could operate alone, then the higher it was the more rapid the deposition would be, and the smaller the grain-size of the resulting deposit. This fact can be noted in the structures of most "still vat" deposits, for the grain-size of the portions next the cathode surface and, therefore, of the portions first deposited and deposited when the cathode layer of the solution was most concentrated, is always, in "still vat" work, of smaller grain-size than the portions formed later when the cathode layers are partly deprived of metal content. In such a case the rapid deposition brings into play powerful factors which operate against it, and do so to such an extent that the normal effect of high current density is masked. One obtains coarse structure in place of fine. It is also true that, as has been shown above, the effect of temperature may be masked.

It is easy to understand how the constant rapid deposition of metal will result in a deposit composed of small grains, just as rapid precipitation of a salt results in crystals of small size. Their concentration being greater, in the case of rapid deposition, the discharged ions (or metal atoms) will have more chance of escaping the attentions of any substances in the solution likely to react with them, and thus render them unavailable for the formation of solid metal; and, further, there will be fewer other molecules present per unit volume to form hindrances (as buffers, so to say) to the tractation of the available metal atoms. Consequently, it will be easier to form nuclei; and the more embryo crystals are formed per unit volume, the smaller the structure will be. A diagram will help here.



. represents an available metal atom.
O represents one or other of the remaining components.

A and B represent projections on the plane of the paper of the contents of unit volumes of two solutions. They can represent equally well unit areas of the solutions at or very close to the cathode surfaces. In A the concentration of the available metal atoms is supposed great; in B it is small. It is easy to see that, on the whole,[1] the atoms will have much more chance to unite one with another in the solution of greater metal atom concentration than in the other. In doing so they will form nuclei, and will not take places in a crystalline aggregate already formed, and thus aid in its growth. No doubt some atoms—those, for instance, that are not sufficiently near together to affect each other—will be drawn into already formed aggregates, and promote the growth of these. This must, indeed, always happen, for, otherwise, the structure would not be visible even with the aid of the microscope; one cannot see an embryo crystal. But, on the whole, more nuclei will be formed, and the growth of already formed aggregates will be less promoted, when the concentration of available metal atoms is great. Observation justifies this conclusion.

FACTORS OF DEPOSITION

In the foregoing the effects of slow and rapid deposition upon the structure of electro-deposited metal have been considered, and the causes of slow and rapid deposition stated. The causes are factors of deposition that determine the grain-size of the deposits. It will now be advisable to consider them and their effects separately, for it is these factors that one can, to a great extent, and must, as far as possible, control, in order to secure a deposit possessing the required structure. The consideration of them will, therefore, be attempted, and illustrations will be given or referred to, in order to make the argument more clear.

The factors of deposition that affect the structures of deposits are, principally, and so far as the author's experience goes: (1) Current density; (2) temperature; (3) movement of electrolyte or electrodes; and (4) the composition of the solution. These, if not the only ones,[2] are certainly those that exercise most action. Each is worthy of consideration.

1. *Current density.* The effect of increase in current density has been stated above. The conclusions derived by Sieverts and Wippelmann from their experiments upon copper (carried out, be it noted, with the employment of a solution agitated by means of a mechanical stirrer) are worth statement in full.[3] They say: "*At the beginning of the electrolysis there is always deposited a thin layer of finely crystalline metal,*[4] which does not adhere to iron cathodes.[5] Then V-shaped crystallites grow out into the electrolyte in a direction approximately perpendicular to the surface of the cathode. The magnitude of these crystallites *diminishes* with *increasing* current density; but if this exceed an amount

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[1] These words—"on the whole"—are inserted to make certain qualifications that may be necessary to the argument. One such is mentioned in the text.

[2] It has been stated by, for instance, W. D. Bancroft, that difference of potential affects the structure of deposits. *Electrochem. Indus.*, 1904, vol. ii. p. 390; *Trans. Am. Electrochem. Soc.*, 1904, vol. vi. p. 27; and *Jour. Phys. Chem.*, 1905, vol. ix. p. 277. See also *Trans. Am. Electrochem. Soc.*, 1913, vol. xxiii. p. 266.

[3] *Op. cit., Zusammenfassung* (1).

[4] The italics are due to the present author.

[5] Cf. Chapter I., p. 6. The solution used was the acid copper bath.

that depends in each case upon the prevailing conditions of deposition, the crystallites again become larger; at the same time the texture (*Gefüge*) becomes more irregular. At high current density all regularity ceases, the structure becomes "unintelligible" (or, "difficult to read": German=*undeutlich*), "and cracks and holes exist in the deposit." The present author, in his paper on iron,[1] says: "Macroscopic and microscopic observations of the deposits . . . seem, therefore, to warrant the following conclusions: (*a*) As the current density rises from 60 amp./ft.^{2} so does the size of grain until—(*b*) a maximum grain-size is reached somewhere in the region of 120 amp./ft.^{2} (*c*) The size of grain then *diminishes* to a minimum which lies somewhere between 120 and 200 amp./ft.^{2} (*d*) It again becomes larger at the highest current densities employed." It is interesting to compare the results of Sieverts and Wippelmann with those of the author. In doing so it must be remembered that, while the former were obtained from experiments on copper in which the temperature did not exceed 30° C. and agitation was used, the author's conclusions were derived from work on iron, conducted in a "still vat" and at a much higher (but uniform) temperature, namely, 110° C. Yet, despite these differences of conditions, the two sets of results are comparable, as will be shown. The German authors agree with the writer upon this, namely, that as current density rises alternations in grain-size occur. They agree, further, in this, namely, that increase in current density does cause increase in grain-size, though it *may* cause a decrease. But whereas the Germans say that they found a *decrease* to occur first, and then, after a certain maximum of current density was reached, an increase, the author found that, first, there was an *increase*, then decrease, followed by another increase. The difference, then, is as to the first increase found by the author to occur. This requires explanation, of course. But, first of all, it must be mentioned that the results obtained by W. Blum and his co-workers [2] are in sufficient agreement with those of Sieverts and Wippelmann. They say (*op. cit.*, p. 165): "With low current density, especially at higher temperatures, the copper possesses a relatively coarse structure, except at the surface where the initial deposition is made. By increasing the current density, *particularly at lower temperature*,[3] the structure assumes a columnar appearance, the crystals being long and finger-like. With still further increase in current density the crystalline structure is much broken up . . ." It is to be noted that the American authors (like the German) used agitation—by compressed air; "agitation by mechanical means has not," they say, "proved satisfactory" for their baths. To return to the above-mentioned difference, the author believes that this is solely due to the use of agitation, and that if agitation had not been employed, then the first decrease in grain-size would not have occurred. In other words, neither Sieverts and Wippelmann nor Blum and his collaborators were, in their experiments on the effect of current density, studying the effect of current density at all; they were noting the combined effect of *two* factors, namely, current density *and* agitation, and, as will be shown below, agitation is such a powerful factor affecting the structure of deposited metal that it often masks the effect produced by others. It has already been explained why, on increasing the current density, coarser structures may be expected to be obtained, as they are in fact obtained, in the absence of other factors powerful enough to disturb or mask the effect produced by current density alone. This is seen in the above-cited results obtained by the author with iron. After a current density of about 120 amp./ft.^{2} was reached, the grain-size was found to diminish. In the author's opinion, this decrease was due to the movement, or considerable increase of it, caused in the bath, at about 120 amp./ft.^{2}, by local thermal changes and " concentration currents " of increased intensity, and also, probably, in some degree, by the increase in hydrogen evolution. If this is so, then the decrease in grain-size is not due to current density alone, but to current density combined with the factor, agitation, just as occurred in the experiments of Sieverts and Wippelmann and of Blum and his co-workers. Only two of the probable causes just mentioned will be dealt with here, and those briefly. It is well known to platers that their solutions become warm after being at work at full load for some time ; and the higher the current employed, the warmer they become. This is due to the combined effect of the electrical resistance of the solution—the so-called " Joule heating "—and the *heat of reaction* (chemical energy). The heating will cause the thermal convection currents to become more vigorous ; and it will do so whether the bath be worked at high or low temperature. It is also well known that the higher the current density, the greater is the liability to hydrogen evolution ; and R. Kremann claims that the movement of the electrolyte caused by hydrogen evolution is responsible for diminution in grain-size.[1] The present author quite agrees that it may be a contributory cause ; but, at the same time, he does not for one moment believe that the diminution in grain-size that occurs in baths containing some excess of free acid is due wholly to hydrogen evolution. Kremann worked with iron-plating baths. As regards the acid copper bath, it is true that when a bath of the usual constitution is used and the current density at which the bath is usually worked is employed, then very little hydrogen indeed is evolved. But when the bath is used as a " still vat," and higher current densities are employed, then certainly hydrogen is evolved. And the explanation is simple. The copper in the cathode layer of the electrolyte becomes quickly used up and, therefore, if the current density remains constant, hydrogen will be liberated ; and this will occur the sooner the higher the current density is. Any diminution in grain-size occurring in the acid copper bath may thus also be due to movement caused by agitation occasioned by the evolution of hydrogen. Both Sieverts and Wippelmann and the author found that after certain current densities were reached (which depended upon the general prevailing conditions and might be different under different conditions), the grain-size began to increase again. The author is of opinion that this increase, or, in his case, second period of increase, is again due to the close connection that exists between the effects of current density and movement. This will be further considered later in the section entitled "Movement."[1]

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[1] *Op. cit.*, p. 16.

[2] *Trans. Am. Electrochem. Soc.*, 1916, vol. xxx. p. 159.

[3] Again the author's italics.

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[1] *Monats. f. Chemie*, 1917, vol. xxxviii. p. 367.

(2) *Temperature.* The way in which increase of temperature may affect the size of the grains of a deposit has been considered, in some measure and incidentally, above. It may help to cause a decrease in grain-size. But the author has found that temperature may cause an increase.[2] Blum has also made a statement to the same effect.[3] The apparent inconsistency between the effects caused by temperature is, without doubt, due to the fact that this variable brings into play factors which may entirely mask any effect it by itself would produce. It is not easy to see how it could be otherwise, assuming that structure is dependent upon concentration of available metal atoms. It is not easy to understand how a few degrees—even a hundred—can so affect the energy of the just discharged and available metal atoms as to have any effect upon their tractations or their arrangement in the space lattice of the crystal. The author believes that what happens is the following sequence: Imagine deposition to be occurring under conditions that are resulting in the formation of large crystalline grains and that, now, the temperature is raised considerably by a definite amount. This rise of temperature will cause thermal convection currents which produce stirring of the electrolyte. Temporarily, at any rate, more metal molecules, and so more metal ions, are, in consequence, brought into the cathode layer. This greater concentration of salt molecules and metal ions results in a greater concentration of available metal atoms. Hence, the opportunity for new centres of crystallization to be formed is greater, and the structure of the deposit is likely to be of smaller grain. The effect of temperature, acting through agitation, is here diminished grain-size. If the current density is not greater than is sufficient to account for all the metal atoms (including the increase due to the movement set up by the increase of temperature) brought to the cathode area, the grain-size will remain smaller; but, if it is more than enough, the increase will occur, because, even in the presence of increased movement, caused by the rise of temperature, the current density will tend to exhaust the cathode layer of its metal content.

3. *Movement.* The importance of movement or agitation in deposition work has been mentioned in a former chapter.[4] There is no dispute about it among practitioners. Whether the agitation be effected by

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[1] The work of Blum and his collaborators is not considered in much detail in this chapter, because, in the author's view, although they purport to adduce experimental evidence in favour of Professor Bancroft's "Axioms" of electro-plating (*vide* references in Note 2, p. 134 above), they do not seem to him to be conclusive, though he would not like to go so far as A. G. Betts, who says in the discussion of their paper (at p. 237) that they do not "seem able to prove very much for them." Such a statement is not to be wondered at, seeing that Blum and his co-workers appear in this paper to consider it sufficient to observe the surface aspects of deposits, and that they are entitled to draw conclusions from such observations alone regarding the effects of the factors of deposition upon structure. A moment's reflection is sufficient to assure one that that is impossible.

[2] Schwarz mentions low temperature as one of the conditions he found necessary for the formation of idiomorphs of deposited copper, *op. cit.*

[3] *Op. cit.*

[4] Chapter IV., p. 39.

movement of the cathode rods, or by blowing air into the solution, or by other means,[1] the practical results are the same, namely, (i) a higher current density can be used and, thus, quicker work done; (ii) a smoother deposit is usually obtained. The causes of these results are well worth careful study; they will now be discussed.

There is a certain maximum of current density that can be used in the cases of all plating solutions, used as "still vats." This may be low, as in the case of the double nickel sulphate bath, or it may be considerable, as in the case of the acid copper bath. In the case of any one metal the maximum varies with the composition of the solution used: it varies, too, with the concentration of the metal salt, in the case of any one electrolyte. Thus, in the case of nickel again, 3 to 4 amp./ft.^{2} is the most that can be used with the double sulphate bath; but 10 to 15 amp./ft.^{2} can be employed where the solution is made with the single salt,[2] the current density varying with the concentration. Suppose, when the maximum current density has been attained in some definite case, agitation is commenced. It will be found that the current density can then be pushed still higher than the "still vat" maximum, and that the deposit remains good, or may be even better. It will be found also that the increase of current density that can be used for a certain degree of agitation is limited. If, now, the agitation be made more violent, the current density employable can be still further increased up to another and higher limit. This connection between the maximum current density employable and the degree of agitation is well known in practice. It has, too, been the subject of laboratory investigation. For instance, in electro-analysis, very high current density has been used, when a rotating cathode in the form of a spiral of platinum wire has been employed.[3] The author has frequently used over 300 amp./ft.^{2} in determinations of copper by electrolysis. In works practice, 100 amp./ft.^{2}, and more, has been used when depositing copper upon rotating mandrils.[4] The most informative investigation of the subject that has been published is that carried out by J. G. Zimmerman.[5] This author's conclusions are concisely summarized as follows (*op. cit.*, p. 246): "The fineness of grain is dependent upon the current density, other things being equal, and the fineness increases with the current density until, at a certain critical value, a powdery deposit will occur. *Increase in the number of revolutions per minute increases the critical current density*, although, whether it is exactly proportional, I have not been able to determine." During the discussion of Zimmerman's paper there occurred a controversy as to the cause of the (apparently) polished state of the surfaces of the deposits he obtained at his critical current densities. Zimmerman maintained that it was due to a burnishing of the deposit by the moving electrolyte. Cowper

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[1] The relative merits of different methods of agitation are discussed in *Trans. Am. Electrochem. Soc.*, 1903, vol. iii. pp. 252 et seq., by Prof. Bancroft, Dr. Hering, and others.

[2] Cf. Chapter VI., p. 59.

[3] Illustrations of such cathodes will be found in any text-book on Electro-analysis. *Vide* A. Classen's *Quantitative Analyse durch Electrolyse.* The complete apparatus is shown in photographs in J. W. Mellor's *Treatise on Chemical Analysis*, p. 257. (Griffin, 1913.)

[4] *Trans. Far. Soc.*, 1905, vol. i. p. 215.

[5] *Trans. Am. Electrochem. Soc.*, 1903, vol. iii. p. 245.

Cole uses the weird expression "skin friction." But Carl Hering objected to this view. He said (p. 251): "I think the correct explanation is that with high current densities the molecular layer of liquid next to and in molecular contact with the cathode is exhausted of its metal before fresh liquid can get there, hence hydrogen or other things will be set free, spoiling the deposit." C. J. Reed, supporting Hering, said: "I do not believe that the friction of the liquid has anything to do with it" (*i.e.*, the "polished" surface). He attributed it *to the increased rate of supply of ions to the cathode.* As a matter of fact, the so-called "polished" surfaces of such deposits are not polished at all in the mechanical sense. There is no Beilby film on the surface such as would be produced by mechanical polishing, whether this is effected by water, electrolyte, or other means. Those who allege the existence of a skin or film upon the surfaces of such deposits as are being considered adduce no evidence in support of their allegation. On the other hand, the author has shown[1] that the surface is almost certainly the result of the smallness of grain which characterizes the structure of deposits formed at high critical current densities. The conclusions expressed in the paper referred to (in Note 1 below) are: "(1) That the 'polished' appearance often observed on the surfaces of deposits formed upon rotating cathodes is due to the smallness of the grains of which the deposits consist; (2) that the smallness of grain is the result of the constancy of metal concentration at the cathode surface; and (3) that, since mechanical movement can maintain constant the metal concentration, rotation of the cathode, which is a mode of mechanical movement, operates in that way in the cases of deposits formed upon rotating cathodes, and not by way of burnishing or the like, as suggested by some other authors" (*op. cit.*, p. 509). Incidentally, the author suggests the following as an interesting piece of research: (*a*) Prepare a number of deposits of (say) copper formed at various critical current densities, but under otherwise similar conditions; (*b*) plot current densities against degree of agitation—peripheral speed of a cylindrical cathode, for instance; and (*c*) prepare micrographs of polished and etched cross-sections of the deposits.

It is apparent that concentration of available metal atoms must here again be the prime factor immediately responsible for the structure of deposits. Current density acts in supplying them by discharge of metal ions, and agitation acts in bringing the metal ions to the surface of the cathode, and thus preventing exhaustion of the cathode layer by the high current densities. Current density and agitation are contributory factors; but concentration of available metal atoms is the determining condition. The importance of movement (whether rotation or by other means) is obvious; the author has shown that even simple to and fro movement of the cathode rod is sufficient to cause great structural differences.[2] The structure resulting from the employment of movement is always more fine-grained than is that of deposits formed in "still vats," but under otherwise similar conditions. The structure is very often fibrous, but not always so. The following example is instructive. Fig. 25 shows the polished and etched surface of a cross-section of a copper deposit formed on a brass rod suspended vertically in the bath. The current density was high, and the rod was moved to and fro during deposition. The structure is obviously fine-grained, but it is not wholly fibrous, as is the structure of an iron deposit shown in a former chapter.[1] The copper deposit has a fine-grained, but broken, structure; much of it is fibrous. The author believes this structure is the result of the current density being too high for the degree of agitation (or better said, perhaps, movement) employed, or, in other words, the current density exceeded the critical value determined by the conditions of deposition that prevailed. Most probably, if the solution had been more concentrated, as regards copper sulphate, the structure would have been wholly fibrous. The type of structure here shown is characteristic of many deposits, and it is a difficult type to interpret, if the connection between current density and movement (here being considered) is not known.

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[1] *Jour. Phys. Chem.*, 1921, vol. xxv. p. 495. Dr. M. von Schwarz' discussion of this paper is of interest. Vide *Zeit. f. Metallkunde*, 1922, vol. xiv. p. 134.

[2] *The Electro-deposition of Iron*, p. 16, Series III. (H.M. Stationery Office).

It is important to notice again here that high current density must be aided by movement, if the grain-size of a deposit is to remain small during any considerable period of deposition. Otherwise from being small near the surface of the cathode it will become large.[2] Movement has so powerful an effect that it may altogether mask that which should be produced by one factor (current density, say) in and by itself. As has been seen, even slight to and fro movement is sufficient to mask the effect of high current density.

4. *Composition of the solution.* It has been noticed how the composition of the solution, as regards the concentration of the metal salt contained in it, may affect the structure of a deposit. This is seen in deposits of other metals, as well as in those of copper. Other components of the solution have important effects upon structure. These will be briefly considered under the headlines: (i) Complex salts; (ii) acid; and (iii) colloids.

(i) *Complex salts.* When copper cyanide and potassium cyanide are dissolved together in water, a substance that has for its formula $K_2Cu(CN)_4$ is formed and can, if proper precautions are taken, be separated out in the solid state as a white powdery compound. Similarly, silver cyanide and potassium cyanide yield $KAg(CN)_2$: this is the salt that forms the essential component of most silver-plating solutions. When such compounds are dissolved in water, they split up, for the most part, into potassium cations and anions which contain the important metal—the copper or silver. There is also a very small number of copper or silver cations present, but not sufficient of them to answer the usual analytical tests for those metals. Such anions are called *complex* ions, and the salts that give rise to them *complex* salts. Such complex salts are by no means always cyanides. There exist complex oxalates, *e.g.* iron ammonium oxalate, $(NH_4)_3Fe(C_2O_4)_3$, and complex chlorides, such as the

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[1] Chapter II., Fig. 3.

[2] Cf. Chapter III., Fig. 8. This deposit (of iron) was formed in a "still vat" and at high current density. Compare Fig. 26, which shows a similar structure in a copper deposit, formed in a "still vat," too, but at low current density.

PLATE XV.

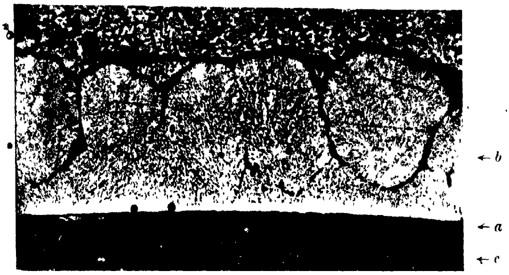

Fig. 25.—Copper deposited on a brass rod. ×90. This is a layer, *a*, of lead deposited between the copper, *b*, and the brass, *c*.

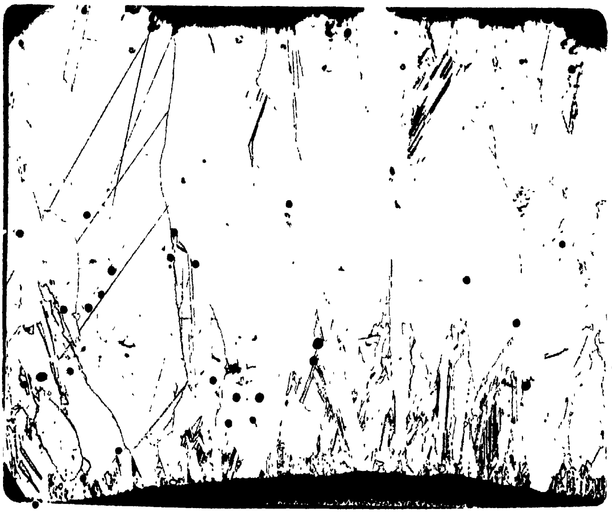

Fig. 26.—A copper deposit showing large-grained structure. ×50. (*Cf.* Fig. 8, Chap. III.)

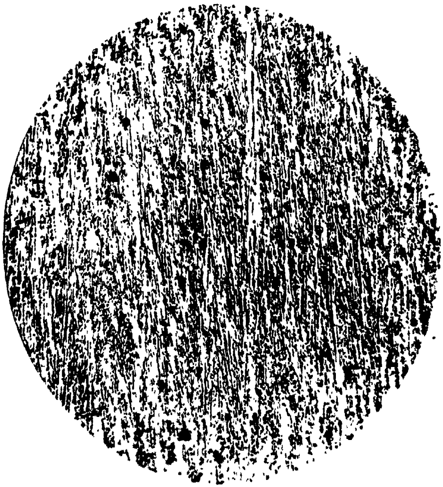

Fig. 27.—A nickel deposit showing very fine-grained structure of the fibrous type. × 450.

platino-chloride of potassium, K_2PtCl_6; but the most important to the electro-plater are the cyanides. The complex salts, yielding complex anions, are so called in order to distinguish them from *double* salts, such as the alums, *e.g.* potash alum, K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$, which do not yield complex anions, but the metal cations K^+ and Al^{+++}, and the well-known sulphanion SO_4^{--}. Such, at any rate, was the old classification: later work has proved that the distinction between the two classes is one rather of degree than of kind.[1] The mechanism of the electrolysis of solutions formed from complex salts has already been briefly considered in the last chapter; the matter of note here is that deposits from such solutions are found to be, so far as they have been studied, always of a fine-grained and, usually, fibrous structure. The author does not pretend to know why that is so. The view taken by Professor Bancroft[2] and some others is that the formation of a "fine-grained deposit is favoured by high current density and potential difference" (between the cathode and the adjacent solution). We know, as regards current density, that, if this is high and there is no agitation employed, the grain-size is large and not small; as regards cathode potential, the fact that this has been found to be high in cases where the grain-size of the deposit is small does not explain the mechanism whereby high potential produces small-grained structure. Quite another view is indicated in the following remarks. As has been pointed out,[3] Pfanhauser regards the ordinary nickel ammonium sulphate solution as containing a complex salt and not a double salt, and explains the electrode reactions on that basis. Certainly, deposits from it have a macroscopic aspect similar to deposits of copper or silver formed in cyanide solutions, and there are those who venture to say that the micro-structure is similar too, though, so far as the author is aware, there is no sufficient evidence of the assertion. At the same time, if the structure of the deposit shown in Fig. 27[4] be studied for a moment, it is clear that the nickel has a very fine and fibrous structure. This deposit was formed in a concentrated solution containing magnesium and nickel sulphates,[5] together with some boric acid, but it was formed under "still vat" conditions and at a comparatively high current density—conditions which, in the case of the acid copper bath and most sulphate of zinc baths, would yield coarse-grained deposits, crystalline in macroscopic aspect. This connection between fibrous (or small-grained) structure and complex salts is curious and interesting.

(ii) *Acid.* The effect produced by free acid in the solution upon the structure of deposits of iron and zinc has been illustrated already.[6] The change in macroscopic aspect caused by adding quite small amounts of dilute acid (HCl) to a small bath of ferrous calcium chloride solution is so rapid that it may, indeed, be referred to as sudden, though this term would not be applicable in the cases of solutions of 100 gals. and more in bulk, where the effect produced by any addition is always shown gradually. While there is no doubt about the cases of iron and zinc just mentioned (the micrographs are conclusive), it is not easy to find in the literature of electro-deposition any direct statement as to whether acid causes any diminution in grain-size in the case of copper.[1] The statements made usually refer to betterment of the deposit without any indication being given as to what the betterment consists in. Does it consist in diminution of grain-size? Blum says: "From the point of view of the plater we may usually define a 'good deposit' as one which is fine-grained, since fineness of grain is in general accompanied by a high lustre, relative freedom from porosity, and comparative hardness."[2] The author is in complete agreement with this statement—with its qualifying adverbs. Further Professor Bancroft states that bad deposits are due to (*inter alia*) excessively large crystals; and Mathers, speaking of lead deposits, says: "An increase in free formic acid to 2 per cent. gave a still better cathode, while with larger amounts of free acid the deposits seemed to become more crystalline and more rough."[3] Therefore, if one accepts as the criterion of a good deposit one that is fine-grained (and this is seen to be true in the cases of iron, zinc, and lead, at least), it is not unfair to assume that the betterment found to occur, in workshop experience, in copper deposits as the amount of sulphuric acid in the bath is increased is due to successive diminution of grain-size, and that the effect of acid is, in the case of copper also, to cause such diminution.

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[1] *Vide* T. S. Moore, in R. A. Lehfeldt's *Electro-chemistry*, p. 133. (Longmans.)

[2] *Trans. Am. Electrochem. Soc.*, 1913, vol. xxiii. p. 266. The following papers should be consulted on this point: H. Stäger, *Helv. Chim. Acta*, 1920, vol. iii. p. 584; V. Kohlschütter and H. Schödl, *ibid.*, 1922, vol. v. p. 490; and F. Förster's *Elektrolyse wäss. Lösungen*, 1922, pp. 384–397.

[3] *Ante*, p. 33.

[4] Cf. Fig. 5. which shows, at higher magnification, the structure of a deposit formed in the same bath.

[5] In such a solution it is highly probable one has a complex magnesium-nickel salt and complex anions containing nickel.

[6] *Vide* Figs. 12, 14, 15, and 20, *ante*. Also see *Trans. Far. Soc.*, 1922, vol. xvii. p. 442.

(iii) *Colloids.* It has already been noticed that the presence of a colloid in the solution is often of advantage (as in the case of zinc), and sometimes necessary (as in the case of lead). There is considerable evidence that the betterment in the deposit is, in this case too, due to the fact that, where colloid is present, the grain-size is cut down; and especially and more markedly is this so, if free acid is also present in the solution. The effect of the presence of colloids is stated as a general proposition by H. J. S. Sand in his recent paper on "The Rôle of Colloids in Electrolytic Metal Deposition,"[4] which contains a citation and discussion of much (but not all) of the work that has been done on the subject. Sand says (p. 347): "Probably in all cases the deposit is rendered more fine-grained," and he adds,—though this is less certain,—". . . and more brittle." The matter will not be pursued further here; but a very interesting example of the effect produced by gelatine (or glue) in zinc deposition may well be given. G. D. Scholl says:[5] "Whenever glue was omitted from the cells for a time, the deposit would become full of holes. This is undoubtedly due to the action of impurities which

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[1] Unless the statements of Sieverts and Wippelmann be considered as such (*op. cit.*).

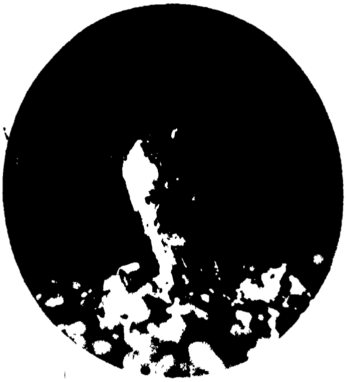
[2] *Trans. Am. Electrochem. Soc.*, 1919; vol. xxxvi. p. 215.

[3] *Ibid.*, 1914, vol. xxvi. p. 127.

[4] See *The Fourth Report on Colloid Chemistry*, 1922, p. 346. (H.M. Stationery Office.)

[5] *Chem. and Met. Eng.*, 1922, vol. xxvi. p. 601. The author is not to be taken as endorsing Scholl's view as to the cause of the betterment he observed.

PLATE XVII.



ig. 28.--An idiomorphic crystal of deposited copper. It shows the edge and angles of a crystal--rounded considerably by concentration currents. × 12.

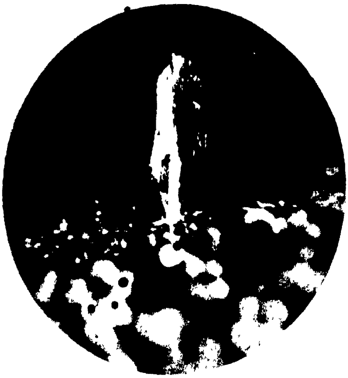


Fig. 29.—As Fig. 28, but showing the crystal on its opposite side. × 12.

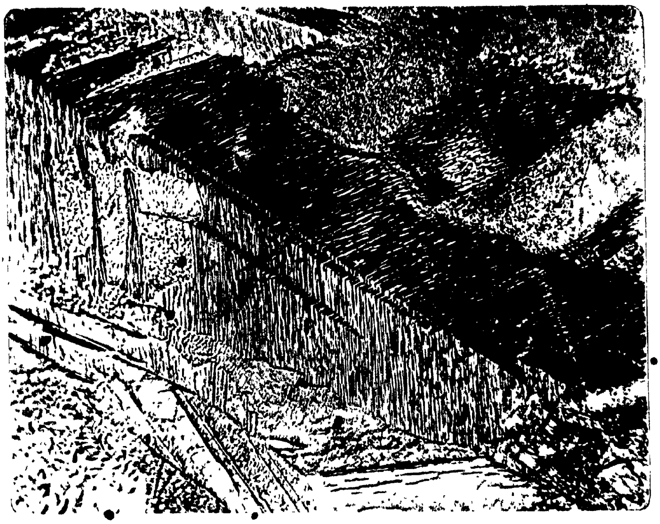


Fig. 30.—A crystalline grain of deposited copper. The photograph shows the internal structure of the grain. It also shows (opposite the arrow) unremoved portions of the "Beilby layer" formed on the surface of the specimen during polishing. It is interesting to note the slip-lines. × 500.

are rendered either inert or retarded in action by the glue. . . . The addition of glue after its total absence for some time causes a marked and almost instant change in the deposit of zinc. In one case the entire cell room was in trouble; the sheets were peppered with holes, and in some cases were actually on the verge of breaking away from the cathodes. Glue was added, and within twenty minutes a change had come over the entire cell room. Re-solution had been arrested, and in the great majority of cases the sheets had actually 'healed' and plating had been resumed." The effects of the presence of complex salts, acid, and colloids, respectively, in a plating solution appear to be each of them the same, namely, diminution of grain-size.

The argument advanced in the foregoing is that concentration of available metal atoms is the all-important factor in the formation of the structure of a deposit. It is hoped that it has been made clear that this proposition is true in, at least, a large number of cases; critics of some of the author's work appear to believe that this view is more generally held than he was or is aware.[1] If it is universally true, then the effects of complex salts and of the other types of substances just mentioned must so act as to bring about quick deposition, and, consequently, the formation of large numbers of nuclei or embryos, and hinder crystal growth. The performance of much more experimental work is necessary before it can be said whether or not that is so; the results of that work will form a crucial test as to the extent to which the hypothesis outlined holds. It does not matter what the outcome of that test is, so long as the truth is known.

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[1] See, e.g., *Engineering*, 1922, vol. cix. p. 303

CHAPTER XII

ON READING

A QUESTION that has been put to the author on many occasions runs—What shall I read?

The first reply that may be given to this inquiry is of a negative nature, namely: Do not read, *in the first instance*, anything that is more than ten years old, except (1) in order to become acquainted with the history of a matter, or (2) where a research is to be followed or engaged upon, in order to find out what others have done in regard to the research contemplated. It is most essential that every one engaged in work on the electro-deposition of metals should keep himself up to date. The practical man—the man in the shop—is, just as is the research worker, likely to waste time and effort, from ignorance of contemporary knowledge, if he consults old and out-of-date books and other sources of information. The author has himself found it to be, in most cases, of most use and benefit to work backwards, so to say. He consults the latest literature *in the first instance*, and then follows up the references given in that. Another piece of advice (given to him by one who knew) that the author has followed with advantage is this: If one wants to obtain information upon some subject of electro-deposition, it is sheer waste of time to consult text-books on chemistry or physics in regard to it. Very few of these books give any useful information upon the subject, and many of them make statements that are harmful because they are wrong. The types of book that should be consulted are (1) those which are concerned with physical chemistry, pure or applied, and (2) technical works on the electrolysis of aqueous solutions.

The periodicals and text-books which the author recommends are as follows:

I. PERIODICALS

(a) ENGLISH (OR AMERICAN)

1. *The Metal Industry*. (New York edition, 99 John Street, New York; and London edition, Bedford Street, Strand, London.)
2. *The Brass World*. (153 Waverley Place, New York.)

   The three foregoing journals are of great interest and use to the practical man, and the research worker will often find them useful.
3. *The Electrician*. (8 Bouverie Street, London.) This journal has done more than any other English paper in the publication of matters relating to the electro-deposition of metals.
4. *Chemical and Metallurgical Engineering*. (McGraw, Hill & Co., Tenth Avenue, at 36th Street, New York; and 8 Bouverie Street, London.)

(b) French

Le Génie Civil. (6 Rue de la Chaussée-d'Antin, Paris.)

(c) German

1. *Zeit. für Elektrochemie.* (W. Knapp, Halle, Germany.)
2. *Zeit. für Metallkunde.* (Verlag des Vereines deutscher Ingenieure, Sommerstrasse 4A, Berlin.)
3. *Elektrochemische Zeitschrift.* (Brandenburgische Buchdruckerei, Mühlenstrasse 9, Berlin-Schöneberg, Germany.)
4. *Stahl und Eisen.* (Verlag Stahleisen, Dusseldorf, Germany.)
5. *Metall. und Erz.* (W. Knapp, Halle, Germany.)

Nos. 1 and 2 are almost indispensable to a man engaged upon research. It is advisable to look through 3, 4, and 5 from time to time. This can be done at a library.

II. TEXT-BOOKS

(a) English

1. *Electro-chemistry*, by R. A. Lehfeld. (Longmans, London.)

   This is the only text-book on the principles of electro-chemistry (apart from their application) published in this country. It is well and clearly written. It is essentially a book for the more advanced student: the man in the workshop will not understand most of it. The present edition is dated 1904, but that need not prevent a student possessing it, always provided he remembers its date and looks up the later literature.

2. *The Principles of Applied Electro-chemistry*, by A. J. Allmand. (Arnold, London.)

   This is the only text-book on its subject published in this country that the author considers to be really valuable. It is comprehensive, and it is reliable, except here and there, on matters of practice.

3. *Practical Electro-chemistry*, by the late Bertram Blount. (Constable, London, 1906.)

   This book treats of the practical side of electro-metallurgical processes, including electro-refining and electro-plating. It is, however, out of date, and should be consulted in a library.

4. *Electric Smelting and Refining*, by W. Borchers. Translated by W. G. M'Millan. (Griffin, London, 1904.)

   This book, too, is out of date, and should be consulted at a library. Professor Borchers has recently informed the author that a new (German) edition is being prepared. The new edition will be worth its price to all electro-metallurgists: it is to be hoped that an English translation will be published—a translation by a practical man.

5. *Electro-plating and Electro-refining*, by Alexander Watt, and edited by Arnold Philip. (Crosby, Lockwood & Co., London.)

6. *A Treatise on Electro-metallurgy*, by W. G. M'Millan, and edited by W. R. Cooper. (Griffin, London, 1919.)

   The two last mentioned are the best books on the practical side of the electro-deposition of metals published in this country and, perhaps, in the English language. Both were written by practical men, and both have been well edited; but both are out of date. When new editions appear, they will be good investments; till then they should be consulted at a library.

7. *The Principles of Electro-deposition—A Laboratory Guide*, by S. Field. (Longmans, 1911.)

   This book is of much use to a student in the laboratory—especially to one working at a technical school. It is not very recent, but that does not so much matter in this case. The book is rather a classroom than a workshop friend, and a good teacher would supply the additions and corrections that time has made necessary.

8. *The Electro-deposition of Metals*, by G. Langbein, and translated by W. T. Brannt. 8th Edition. 1920. (Published in this country by the Oxford Technical Publications.)

This book has been reviewed for the *Journal of the Institute of Metals*, (vide *Jour. Inst. Metals*, 1920, No. 2, vol. xxiv. p. 513.)

(*b*) FOREIGN BOOKS

Among the foreign text-books that are of value to those engaged in metal deposition, those mentioned in the notes to the text of this book must be included. Most of them are out of date, just as most of the English books are, and, like these, they must be used with caution. A notable exception in this respect is:

Elektrochemie wässeriger Lösungen, by F. Förster. (Barth, Leipzig. 1922.)

No research man can afford to be without this book. It can be purchased for the extraordinarily low price of 14s. "It would be a very desirable thing if somebody were to translate this book, because it is quite in a class by itself" (Prof. W. D. Bancroft, writing in the *Jour. Phys. Chem.*, 1922, vol. xxvi. p. 494). The author agrees that a translation is greatly needed, but the translation would be best done by a number of men, each a master of the subject-matter of the particular section or sections of the book he undertook to translate.

III. ORIGINAL PAPERS

A considerable number of references to papers comprising the results of research have been cited in the notes to the text. This has been done of set purpose. One of the most valuable features of any book on a technical subject is, in the author's opinion, the direction of the reader's attention to the sources where he can obtain first-hand information. Professor Walker has well said: " . . . it is of the utmost importance that even beginners in physical chemistry should become acquainted at first-hand with original work. . . ." The papers cited do not, of course, cover the whole of the literature, but it is believed they comprise the most important ones, and that they will set the worker well on his way.

TABLES

TABLE VIII.

ACCORDING to *Scientific Paper*, No. 275, Bureau of Standards, Washington, the effect on the density of an electrolyte of 1 gram per litre of $CuSO_4.5H_2O$ is practically identical with that produced by 1 gram per litre of H_2SO_4. Therefore, if the density of a solution containing these two substances is known, the amount of the two in grams per litre is also known. And, if the amount of either is determined, that of the other may be found by difference. In Table VIII. the effect of the substances is given.

DENSITY—COMPOSITION RELATIONS IN COPPER SULPHATE ELECTROLYTES

25° C.		40° C.	
Density.	Grms./lit. $CuSO_4.5H_2O + H_2SO_4$	Density.	Grms./lit. $CuSO_4.5H_2O + H_2SO_4$
1·01	20	1·01	26
1·02	36	1·02	43
1·03	52	1·03	60
1·04	68	1·04	76
1·05	84	1·05	93
1·06	100	1·06	110
1·07	117	1·07	127
1·08	133	1·08	144
1·09	150	1·09	161
1·10	166	1·10	178
1·11	183	1·11	195
1·12	200	1·12	212
1·13	217	1·13	229
1·14	234 = 20·5% by wt.	1·14	247
1·15	251 = 21·8 ,,	1·15	265
1·16	268 = 23·1 ,,	1·16	282
1·17	286 = 24·5 ,,	1·17	300
1·18	303 = 25·7 ,,	1·18	318
1·19	321 = 27·0 ,,	1·19	336
1·20	339 = 28·3 ,,	1·20	354
1·21	357	1·21	372
1·22	375	1·22	390
1·23	393	1·23	408

N.B.—The above is taken from *The Engineering and Mining Journal* (New York), June 16, 1917.

TABLE IX

COMPARISON OF THERMOMETRIC SCALES

Cent.	Fahr.	Cent.	Fahr.	Cent.	Fahr.
100	212	69	156·2	38	100·4
99	210·2	68	154·4	37	98·6
98	208·4	67	152·6	36	96·8
97	206·6	66	150·8	35	95·0
96	204·8	65	149·0	34	93·2
95	203·0	64	147·2	33	91·4
94	201·2	63	145·4	32	89·6
93	199·4	62	143·6	31	87·8
92	197·6	61	141·8	30	86·0
91	195·8	60	140·0	29	84·2
90	194·0	59	138·2	28	82·4
89	192·2	58	136·4	27	80·6
88	190·4	57	134·6	26	78·8
87	188·6	56	132·8	25	77·0
86	186·8	55	131·0	24	75·2
85	185·0	54	129·2	23	73·4
84	183·2	53	127·4	22	71·6
83	181·4	52	125·6	21	69·8
82	179·6	51	123·8	20	68·0
81	177·8	50	122·0	19	66·2
80	176·0	49	120·2	18	64·4
79	174·2	48	118·4	17	62·6
78	172·4	47	116·6	16	60·8
77	170·6	46	114·8	15	59·0
76	168·8	45	113·0	14	57·2
75	167·0	44	111·2	13	55·4
74	165·2	43	109·4	12	53·6
73	163·4	42	107·6	11	51·8
72	161·6	41	105·8	10	50·0
71	159·8	40	104·0		
70	158·0	39	102·2		

To convert—

° *C. into* ° *F.*, multiply by 9, divide by 5, and add 32.

° *F. into* ° *C.*, subtract 32, multiply by 5, and divide by 9.

TABLE X

COMPARATIVE TABLE OF SPECIFIC GRAVITIES AND HYDROMETER DEGREES—BEAUMÉ AND TWADDLE

Spec. Grav. at 59° F.	Deg. Bé.	Deg. Tw.	Spec. Grav. at 59° F.	Deg. Bé.	Deg. Tw.
1000	0	0	1245	28·4	49
1005	0·7	1	1250	28·8	50
1010	1·4	2	1255	29·3	51
1015	2·1	3	1260	29·7	52
1020	2·7	4	1265	30·2	53
1025	3·4	5	1270	30·6	54
1030	4·1	6	1275	31·1	55
1035	4·7	7	1280	31·5	56
1040	5·4	8	1285	32·0	57
1045	6·0	9	1290	32·4	58
1050	6·7	10	1295	32·8	59
1055	7·4	11	1300	33·3	60
1060	8·0	12	1305	33·7	61
1065	8·7	13	1310	34·2	62
1070	9·4	14	1315	34·6	63
1075	10·0	15	1320	35·0	64
1080	10·6	16	1325	35·4	65
1085	11·2	17	1330	35·8	66
1090	11·9	18	1335	36·2	67
1095	12·4	19	1340	36·6	68
1100	13·0	20	1345	37·0	69
1105	13·6	21	1350	37·4	70
1110	14·2	22	1355	37·8	71
1115	14·9	23	1360	38·2	72
1120	15·4	24	1365	38·6	73
1125	16·0	25	1370	39·0	74
1130	16·5	26	1375	39·4	75
1135	17·1	27	1380	39·8	76
1140	17·7	28	1385	40·1	77
1145	18·3	29	1390	40·5	78
1150	18·8	30	1395	40·8	79
1155	19·3	31	1400	41·2	80
1160	19·8	32	1405	41·6	81
1165	20·3	33	1410	42·0	82
1170	20·9	34	1415	42·3	83
1175	21·4	35	1420	42·7	84
1180	22·0	36	1425	43·1	85
1185	22·5	37	1430	43·4	86
1190	23·0	38	1435	43·8	87
1195	23·5	39	1440	44·1	88
1200	24·0	40	1445	44·4	89
1205	24·5	41	1450	44·8	90
1210	25·0	42	1455	45·1	91
1215	25·5	43	1460	45·4	92
1220	26·0	44	1465	45·8	93
1225	26·4	45	1470	46·1	94
1230	26·9	46	1475	46·4	95
1235	27·4	47	1480	46·8	96
1240	27·9	48	1485	47·1	97

TABLE X—*continued*

Spec. Grav. at 59° F.	Deg. Bé	Deg. Tw.	Spec. Grav. at 59° F.	Deg. Bé.	Deg. Tw.
1490	47·4	98	1680	58·4	136
1495	47·8	99	1685	58·7	137
1500	48·1	100	1690	58·9	138
1505	48·4	101	1695	59·2	139
1510	48·7	102	1700	59·5	140
1515	49·0	103	1705	59·7	141
1520	49·4	104	1710	60·0	142
1525	49·7	105	1715	60·2	143
1530	50·0	106	1720	60·4	144
1535	50·3	107	1725	60·6	145
1540	50·6	108	1730	60·9	146
1545	50·9	109	1735	61·1	147
1550	51·2	110	1740	61·4	148
1555	51·5	111	1745	61·6	149
1560	51·8	112	1750	61·8	150
1565	52·1	113	1755	62·1	151
1570	52·4	114	1760	62·3	152
1575	52·7	115	1765	62·5	153
1580	53·0	116	1770	62·8	154
1585	53·3	117	1775	63·0	155
1590	53·6	118	1780	63·2	156
1595	53·9	119	1785	63·5	157
1600	54·1	120	1790	63·7	158
1605	54·4	121	1795	64·0	159
1610	54·7	122	1800	64·2	160
1615	55·0	123	1805	64·4	161
1620	55·2	124	1810	64·6	162
1625	55·5	125	1815	64·8	163
1630	55·8	126	1820	65·0	164
1635	56·0	127	1825	65·2	165
1640	56·3	128	1830	65·5	166
1645	56·6	129	1835	65·7	167
1650	56·9	130	1840	65·9	168
1655	57·1	131	1845	66·1	169
1660	57·4	132	1850	66·3	170
1665	57·7	133	1855	66·5	171
1670	57·9	134	1860	66·7	172
1675	58·2	135			

CONVERSION FORMULÆ

1. *Beaumé and Spec. Grav.*

$$\frac{144}{144-\text{Bé}}=\text{Spec. Grav.}$$

This formula applies to liquids having a spec. grav. greater than that of water.

2. *Twaddle and Spec. Grav.*

$$\frac{\text{Spec. grav.}-1000}{5}={}^{\circ}\ \text{Twaddle.}$$

TABLE XI

SPECIFIC GRAVITY OF SULPHURIC ACID

	100 pts. by wt. contain in chem. pure acid	1 litre contains in chem. pure acid	Sp. gr. at 15° C. / 4°	100 pts. by wt. contain in chem. pure acid	1 litre contains in chem. pure acid
	Per cent. H_2SO_4	Kg. H_2SO_4		Per cent. H_2SO_4	Kg. H_2SO_4
05	0·83	0·008	1·225	30·48	0·373
10	1·57	0·016	1·230	31·11	0·382
15	2·30	0·023	1·235	31·70	0·391
20	3·03	0·031	1·240	32·28	0·400
25	3·76	0·039	1·245	32·86	0·409
30	4·49	0·046	1·250	33·43	0·418
35	5·23	0·054	1·255	34·00	0·426
40	5·96	0·062	1·260	34·57	0·435
45	6·67	0·071	1·265	35·14	0·444
50	7·37	0·077	1·270	35·71	0·454
55	8·07	0·085	1·275	36·29	0·462
060	8·77	0·093	1·280	36·87	0·472
065	9·47	0·102	1·285	37·45	0·481
070	10·19	0·109	1·290	38·03	0·490
075	10·90	0·117	1·295	38·61	0·500
080	11·60	0·125	1·300	39·19	0·510
085	12·30	0·133	1·305	39·77	0·519
090	12·99	0·142	1·310	40·35	0·529
095	13·67	0·150	1·315	40·93	0·538
100	14·35	0·158	1·320	41·50	0·548
105	15·03	0·166	1·325	42·08	0·557
110	15·71	0·175	1·330	42·66	0·567
115	16·36	0·183	1·335	43·20	0·577
·120	17·01	0·191	1·340	43·74	0·586
·125	17·66	0·199	1·345	44·28	0·596
·130	18·31	0·207	1·350	44·82	0·605
·135	18·96	0·215	1·355	45·35	0·614
·140	19·61	0·223	1·360	45·88	0·624
·145	20·26	0·231	1·365	46·41	0·633
·150	20·91	0·239	1·370	46·94	0·643
·155	21·55	0·248	1·375	47·47	0·653
·160	22·19	0·257	1·380	48·00	0·662
·165	22·83	0·266	1·385	48·53	0·672
·170	23·47	0·275	1·390	49·06	0·682
·175	24·12	0·283	1·395	49·59	0·692
1·180	24·76	0·292	1·400	50·11	0·702
1·185	25·40	0·301	1·405	50·63	0·711
1·190	26·04	0·310	1·410	51·15	0·721
1·195	26·68	0·319	1·415	51·66	0·730
1·200	27·32	0·328	1·420	52·15	0·740
1·205	27·95	0·337	1·425	52·63	0·750
1·210	28·58	0·346	1·430	53·11	0·759
1·215	29·21	0·355	1·435	53·59	0·769
1·220	29·84	0·364	1·440	54·07	0·779

TABLE XI—*continued*

Sp. gr. at $\frac{15^\circ\,\text{C.}}{4^\circ}$	100 pts. by wt. contain in chem. pure acid	1 litre contains in chem. pure acid	Sp. gr. at $\frac{15^\circ\,\text{C.}}{4^\circ}$	100 pts. by wt. contain in chem. pure acid	1 litre contains in chem. pure acid
	Per cent. H_2SO_4	Kg. H_2SO_4		Per cent. H_2SO_4	Kg. H_2SO_4
1·445	54·55	0·789	1·645	72·40	1·192
1·450	55·03	0·798	1·650	72·82	1·202
1·455	55·50	0·808	1·655	73·23	1·212
1·460	55·97	0·817	1·660	73·64	1·222
1·465	56·43	0·827	1·665	74·07	1·232
1·470	56·90	0·837	1·670	74·51	1·245
1·475	57·37	0·846	1·675	74·97	1·256
1·480	57·83	0·856	1·680	75·42	1·267
1·485	58·28	0·865	1·685	75·86	1·278
1·490	58·74	0·876	1·690	76·30	1·289
1·495	59·22	0·885	1·695	76·73	1·301
1·500	59·70	0·896	1·700	77·17	1·312
1·505	60·18	0·906	1·705	77·60	1·323
1·510	60·65	0·916	1·710	78·04	1·334
1·515	61·12	0·926	1·715	78·48	1·346
1·520	61·59	0·936	1·720	78·92	1·357
1·525	62·06	0·946	1·725	79·36	1·369
1·530	62·53	0·957	1·730	79·80	1·381
1·535	63·00	0·967	1·735	80·24	1·392
1·540	63·43	0·977	1·740	80·68	1·404
1·545	63·85	0·987	1·745	81·12	1·416
1·550	64·26	0·996	1·750	81·56	1·427
1·555	64·67	1·006	1·755	82·00	1·439
1·560	65·08	1·015	1·760	82·44	1·451
1·565	65·49	1·025	1·765	82·88	1·463
1·570	65·90	1·035	1·770	83·32	1·475
1·575	66·30	1·04[illegible]	1·775	83·90	1·489
1·580	66·71	1·054	1·795	8[illegible]·30	1·549
1·585	67·13	1·064	1·800	86·90	1·564
1·590	67·59	1·075	1·805	87·60	1·581
1·595	68·05	1·085	1·810	88·30	1·598
1·600	68·51	1·096	1·815	89·05	1·621
1·605	68·97	1·107	1·820	90·05	1·639
1·610	69·43	1·118	1·821	90·20	1·643
1·615	69·89	1·128	1·822	90·40	1·647
1·620	70·32	1·139	1·823	90·60	1·651
1·625	70·74	1·150	1·824	90·80	1·656
1·630	71·16	1·160	1·825	91·00	1·661
1·635	71·57	1·17[illegible]	1·826	91·25	1·666
1·640	71·99	1·181			

TABLE XII

Specific Gravity of Nitric Acid

Sp. gr.	100 pts. contain at 15° C. grms. HNO_3	Sp. gr.	100 pts. co 15° C. grm
1·007	1·5	1·221	35·5
1·014	2·6	1·231	37·0
1·022	4·0	1·242	38·6
1·029	5·2	1·252	40·2
1·036	6·3	1·261	41·5
1·044	7·6	1·275	43·5
1·052	9·0	1·285	45·0
1·060	10·2	1·298	47·1
1·067	11·4	1·309	48·6
1·075	12·7	1·321	50·7
1·083	14·0	1·334	52·9
1·091	15·3	1·346	55·0
1·100	16·8	1·359	57·3
1·108	18·0	1·372	59·6
1·116	19·4	1·384	61·7
1·125	20·8	1·398	64·5
1·134	22·2	1·412	67·5
1·143	23·6	1·426	70·6
1·152	24·9	1·440	74·4
1·161	26·3	1·454	78·4
1·171	27·8	1·470	83·0
1·180	29·2	1·485	87·1
1·190	30·7	1·501	92·6
1·199	32·1	1·516	96·0
1·210	33·8	1·524	98·0

On a Use for Sulphuric and Nitric Acids in the Plating Shop.—One of the uses for sulphuric and nitric acids in the plating shop is as "dips" for cleaning articles (especially those of brass and copper) before plating them. They are used as a mixture for this purpose and the mixture of acids is known in the trade as "akey" (*vide* Chap. IV., Table 1, p. 43). The nitric acid (which is often called "nitrous" acid in the trade) is the active component: the function of the sulphuric acid is to act as a diluent. A good dip is made by pouring slowly, and stirring the while, 147 parts by weight of sulphuric acid (often referred to as "oil of vitriol") of specific gravity 120° Twaddle, into 33 parts by weight of nitrous acid of specific gravity 74° Twaddle. The mixture must be thoroughly stirred and allowed to cool before being used.

TABLE XIII

PER CENT. COMPOSITION OF PLATING SALTS

Metal Salt.	Formula.	Metal per cent.
Chevreul's salt	$Cu_2SO_3CuSO_3 2H_2O$	49·3
Copper carbonate (basic)	$CuCO_3Cu(OH)_2$	57·48
Copper sulphate	$CuSO_4.5H_2O$	25·46
Copper cyanide (cuprous)	$Cu_2(CN)_2$	70·97
Copper potass. cyanide	$K_2Cu_2(CN)_4$	22 4
Copper trisalt	$Cu_2(CN)_2.4KCN.K_2SO_3$	21·2
Zinc carbonate (basic)	$ZnCO_3.Zn(OH)_2$	29·05
Zinc carbonate	$ZnCO_3$	52·15
Zinc sulphate	$ZnSO_4.7H_2O$	22·74
Zinc cyanide	$Zn(CN)_2$	55·69
Zinc trisalt	$Zn(CN)_2.2KCN.K_2SO_3$	15·5
Zinc chloride	$ZnCl_2$	47·96
Nickel carbonate	$NiCO_3$	49·44
Nickel carbonate (basic)	$NiCO_3.4NiO.5H_2O$	57·87
Nickel sulphate	$NiSO_4.6H_2O$	22·32
Nickel sulphate	$NiSO_4 7H_2O$	21·24
Nickel ammon. sulphate	$NiSO_4.(NH_4)_2SO_4.6H_2O$	14·85
Nickel chloride	$NiCl_2.6H_2O$	24·09
Ferric chloride	Fe_2Cl_6	—
Ferrous chloride	$FeCl_2.4H_2O$	28
Ferrous sulphate	$FeSO_4.7H_2O$	22·8
Ferrous ammon. sulphate	$FeSO_4.(NH_4)_2SO_4.6H_2O$	14·62
Stannous chloride	$SnCl_2.2H_2O$	52·66
Lead acetate	$Pb(C_2H_3O_2)_2.3H_2O$	54·61
Lead perchlorate	$Pb(ClO_4$	45·01
Lead carbonate	$2PbCO_3.Pb(OH)_2$	26·74

NOTE

All the basic carbonates are variable in composition. A general formula for those of the divalent metals, *e.g.*, copper, zinc, nickel, is $xM(OH)_2.yMCO_3$, where M stands for metal, and x and y for varying numbers. Those formulæ and percentages given in Table XIII. are those attaching to the salts most usually found in plating shops (*vide* Chap. X., p. 113, Note 5). A similar remark applies, though less generally, to the cyanides of the metals—especially copper cyanide.

TABLE XIV

SOME CHEMICAL AND ELECTRO-CHEMICAL VALUES

Metal.	Symbol.	At. Wt.	Equiv. Wt.	Electro-chem. Equiv.	Wt. deposited per amp.-hr.	Thickness deposited per hour by 1 amp./dcm.[2]
				mg.[1]	grms.	mm.
Nickel . .	Ni··	59	29·5	0·304	1·094[2]	·0129
Cobalt . .	Co··	59	29·5	0·305	1·099[3]	·0126
Iron (*ferrous*)	Fe··	56	28	0·290	1·042[2]	·0128
Zinc . .	Zn··	65	32 5	0·339	1·219[2]	·0171
Chromium .	Cr···	52·5	17·5	0 182	0·6519[3]	·0093
Tin— (stannous)	Sn··	118	59	0·618	2·119[3]	·0302
Copper—						
(*cupric*) .	Cu··	63·5	31·7	0 3289	1·186[2]	·0133
(*cuprous*) .	Cu·		63·5	0 657	2 372	·0265
Silver . .	Ag	108	108	0·1118	4·023[2]	·0380
Lead . .	Pb	207	103·5	0·071	3·857[2]	·0338

NOTES

1. "*The Chemical Equivalent* of an element is defined as that amount of it which combines with or takes the place of 1 part (strictly 1·008 parts) by weight of hydrogen (or 8 parts by weight of oxygen)."—G. Senter, *Text-book of Inorganic Chemistry*, 1911, p. 121.

2. *The Electro-Chemical Equivalent* of a substance is the amount of it deposited by 1 coulomb (*i.e.*, 1 ampère flowing for 1 second) of electricity.

3. None of the numbers given in Table XIV. is strictly accurate—not even those representing the atomic weights. But they are sufficiently near to correct values for all practical (workshop) purposes. If at any time the reader should, for some special purpose, require greater accuracy, he should consult one of the standard text-books referred to in the notes to this book, *and he should take care that the book used is of the latest date.*

[1] All values in this column (except those for tin and monovale
from W. Löb, *Leitfaden der praktischen Elektrochemie*, 1899, Table 1, p. 235.

[2] From A. J. Allmand, *Practical Electro-chemistry*.

[3] From Watt and Philip, *Electro-plating*, 1902, Table 9, p. 656.

TABLE XV

EQUIVALENTS

There are a number of equivalents that those engaged in the electro-deposition of metals have frequently to make use of. They are given here.

1 ounce (avdp.) = 28·35 grammes.
1 gallon (Imp.) = 4·5436 litres = 4543 cubic centimetres.
1 „ (U.S.) = 3·785 litres.
1 „ (Imp.) = 10 lb. (English).
1 „ (Imp.) = 8 pints = 32 gills = 160 ounces = 4 kilogrammes 540 grammes,

and conversely,

1 litre = 100 centilitres = 1 cub. decimetre = 1·76 Imperial pint.
= 2·114 U.S. pints.

INDEX

Acid, effect in plating solutions, 54, 77, 132, 141.
Adams' double nickel salts solution, 3, 59.
Addition agents, 33.
,, in lead baths, 88 et seq.
,, in tin baths, 99.
,, in zinc baths, 71, 73.
Agitation, effect on structure of, 55, 137.
,, employment of, 39.
" Akey," 43, 1[illegible].
Anodes, 37.
,, disintegration of copper, 120.
,, for chromium deposition, 109.
,, iron, 50.
,, nickel, 64, 68.
,, tin, 104.

Bancroft (W. D.)—Function of colloids, 34, 72, 142.
,, Use of chromium deposition, 106.
Barth (A.)—Action of electric cleaner, 24.
Black nickel, 59.
Blum (W.)—Structure of deposited copper, 135.
Boracic acid, use in nickel baths of, 62.
,, use in zinc, 73.
Burgess (C. F.)—Sulphuric acid test for zinc deposits, 81.

Caustic soda test for zinc deposits, 82.
Chevreul's salt, 112.
Chromium, electro-deposited, uses of, 10[illegible].
,, ,, properties of, 109.
,, electro-deposition of, literature of, 106.
Classen (A.)—Reactions in the alkaline copper bath, 115.
Cleaning, 21 et seq.
,, examples of, 29.
,, methods of, 43.
,, ,, electro-chemical, 24.
,, ,, mechanical and chemical, 23.
,, practical notes on, 42.
Cobalt, Kalmus' experiments on the deposition of, 5.
,, neglect of, 4.
Colloids, effect on structure of (and of addition agents), 142.
Complex salts, effect on structure of, 140.
Composition of solution and structure, 140.
Copper, disintegration of electrolytic, 120.
,, electro-deposited, structure of, 127.
,, electro-deposition of, solutions for, 6, 7, 112 et seq.
Copper-plating, defects of, 118, 121.
Copper sulphate test for zinc deposits, 80.
Crystallization, laws of, 128.
Current density and structure, 134.

Deposition, factors of, 134.
,, in practice, rules for, 36 et seq.
Deposits, general characters of, 35.
,, structure of, 128 et seq.
Double salts, definition of, 141.
Drying out, process of, 40.

Electro-chemical cleaning, 24.
Electrode efficiencies, 23, 35.
Electro-galvanizing, 5, 69.
Electrolytic dissociation, theory of, 14.
Electron theory, 124.
Electro-plating, general review of, 2 et seq.
Electro-refining, general review of, 1.

Factors of deposition, 134.
,, effect on structure of, 134.
Faraday's laws, 11.
,, practical importance of, 12.
Field (S.)—Reactions of acid copper bath. 123.
,, Zinc extraction by electrolysis, 1.
Finishing deposits, 41.

Gelatin, effect in plating solutions of, 34.
,, use in Betts' lead-plating bath of, 91 et seq.

Hinrichs (G.)—Theory of Ionization, 17, 126.

Ionic theory, 14.
Ionization, Hinrichs' views on, 17, 126.
,, Clausius' and Arrhenius' views on, 14.
Ions, Faraday's definitions of, 11.
Iron, electro-deposited, properties of, 46.
,, ,, structure of, 54.
,, ,, use and applications of 45.
,, electro-deposition of, 48.
,, ,, baths for the, 48, 51.
,, ,, general rules of practice in, 53.

Kalmus (H. T.)—Experiments on cobalt deposition, 5.

Langbein-Fischer iron solution, 48.
Lead, electro-deposited, and corrosion, [illegible].
,, ,, applications of, 86.
,, ,, etching, 95.
,, ,, properties of, 87.
,, ,, structure of, 95.
,, ,, testing for porosity, 95.
,, electro-deposition of, solutions for the, 8[illegible].
,, ,, Betts' solution for the, 91.
,, ,, Mathers' solution for the, 89.
Lehmann (O.)—On the structure of deposited metal, 105.

Mathers (F. C.)—Experiments on copper cyanide solutions, 116.
,, Lead perchlorate bath, 89.
,, Tin oxalate bath, 102.
Mechanical tests for deposits, 78.
Microscope, study of deposits with the, 18.

Neumann (B.)—Glaser's experiments on chromium deposition, 106.
Nickel ammonium sulphate, percentage metal in, 60.
" " solubility of, 6[illegible].
" " solution, comparison with modern baths. 4. 59. 60.
" " solution, reactions of the, 33.
" " solution, remarks on the, 4
" anodes, 64.
" electro-deposited, and corrosion, 56.
" " defects of, 66.
" " properties of, 58.
" " thick deposits of, 58.
" electro-deposition of, 59.
" " solutions for the, 61, 63.
" solutions, boracic acid in, 62.
" " magnesium sulphate in, 63.

Ohm's law, 11.
Oxidized " copper, [illegible].
" tin, 8, 98.

Paweck (W.)—Boracic acid in zinc solutions, 73.
Pfanhauser (W.)—Reactions in double nickel bath, 3
Plating solutions, agitation of, 39.
" composition of, 35.
" upkeep of, 38.
Polishing, nature of, 41.

Quick deposition, effect on structure of, 132.

Reed (C. J.)—Electro-pickle, 26.

Salt spray test, 83.
Salts, conducting, 32.
Salzer's patents, 106.
Sapojnikoff (A. B.)—Structure of deposited metal, 105.
Sargent (G. J.)—Experiments on chromium, 107.
Schlötter (M.)—Adhesion of deposits, 22.
" Iron solution, 51.
" Nickel anodes, 6[illegible].
Schwarz (M. v.)—Structure of deposited copper, 129, 132.
Sieverts (A.) and Wippermann (W.)—Structure of copper,
Slow deposition, effect on structure of, 129.
Structure of deposited metal, 18, 120 et seq.
Sulphites, functions of, 114.
Sulphuric acid test for zinc deposits, 8[illegible].
Supersaturation, meaning of, 12[illegible].

Temperature, effect on structure of, 137.
Theory of electrolytic dissociation, 14
" of electrons, 124.
Tin anodes, 104.
" electro-deposited, and corrosion, 97.
" " properties of, 98.
" " structure of, 104.
" " use and applications of, 97.
" electro-deposition of, 99.
" " solutions for the, 99 et seq.
" salts, 100.

Walker (W. H.)—Caustic-soda test, 82.
Weston (E.)—Use of boracic acid in nickel solutions, 62.
Wippelmann (W.) and Sieverts (A.)—Structure of copper, 130, 134.

Zimmermann (J. G.)—Structure of copper deposits, 138.
Zinc, electro-deposited, and corrosion, 69.
,, ,, properties of, 70.
,, ,, structure of, 76.
,, ,, tests of, 78.
,, extraction by electrolysis, 2.
,, plating, solutions for, 70.
,, ,, use of, 69.

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